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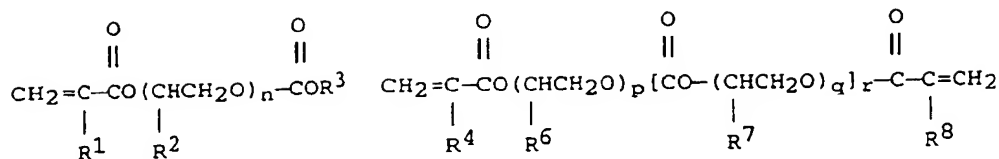
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(54) **NOVEL ACRYLATES, NOVEL ALLYL ETHERS, NOVEL ALLYL CARBONATES, ACRYLATE POLYMERS, ALLYL ETHER POLYMERS, ALLYL CARBONATE POLYMERS, AND SOLID POLYELECTROLYTES**

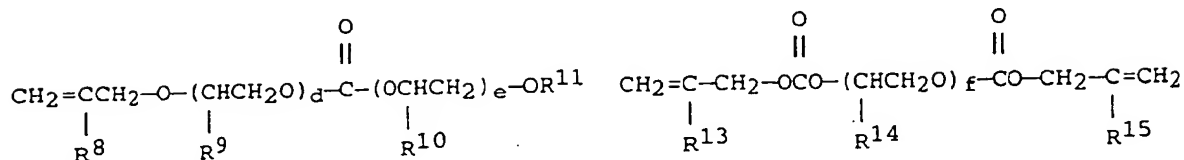
(57) The novel acrylic ester, allyl ether and allyl carbonate of the present invention are characterized by having the structures represented by the following general formulae (I) to (IV):

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(I)

(II)



(III)

(IV)

The above acrylic ester, allyl ether and allyl carbonate are used as a starting monomer which forms a polymer matrix for use in a polymeric solid electrolyte.

The novel polymer of the present invention comprises structural units derived from at least one compound selected from a group of the compounds represented by the above general formulae (I) to (IV). The polymeric solid electrolyte comprising the above novel polymer as a polymer matrix exhibits high ionic conductivity and is chemically stable.

The polymeric solid electrolyte comprising the above novel polymer as a matrix exhibits high ionic conductivity and is electrochemically stable, so that it can be used in, for example, an electrochemical element such as a primary battery, a secondary battery, a capacitor or an electrochromic display and a medical actuator.

Description

TECHNICAL FIELD

The present invention relates to novel polymers employed for purposes such as a polymer matrix of polymeric solid electrolyte and to a process for producing the same. The present invention also relates to a polymeric solid electrolyte for use in a primary battery, a secondary battery, a capacitor and the like.

BACKGROUND ART

It is common to employ a liquid electrolyte in an electrochemical element such as a primary battery, a secondary battery or a capacitor. However, the liquid electrolyte has drawbacks in that liquid leakage occurs and it cannot ensure long-term reliability.

The use of a solid electrolyte for overcoming the above drawbacks of the liquid electrolyte is known. The application of the solid electrolyte to the above electrochemical element enables not only providing an element which is free from liquid leakage and ensures high reliability but also realizing miniaturization and weight reduction of the element per se.

A variety of polymeric solid electrolytes have been studied for recent years. The polymeric solid electrolytes not only are so flexible that appropriate application can be made irrespective of a volume change which occurs during the ion/electron exchange reaction between the electrode and each polymeric solid electrolyte but also has the above-mentioned general advantages of the solid electrolytes.

The use of a complex composed of a polyethylene oxide having polyether structure and an alkali metal salt such as a lithium salt is known among such a variety of polymeric solid electrolytes.

Japanese Patent Laid-open Publication No. 25353/1993 describes a polymeric solid electrolyte composed mainly of a crosslinked resin comprising a copolymer of a polyoxyalkylene diester compound, a polymethoxyoxyalkylene ester compound and an oxy compound having double bond, and an inorganic salt. Further, Japanese Patent Laid-open Publication No. 223842/1994 describes a polymeric solid electrolyte composed of an organic polymer having a carbonate group as a functional group and a metal salt.

However, these solid electrolytes generally have lower ionic conductivity than those of the liquid electrolytes, so that it is difficult to obtain a primary or secondary battery having excellent discharge characteristics therefrom.

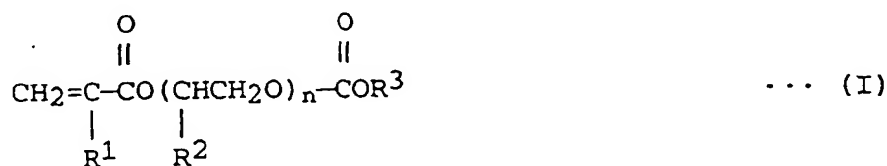
Under the circumstance, there are demands on the development of a polymeric solid electrolyte which can satisfy the requirements such as high ionic conductivity and high electrochemical stability, and the development of a novel polymer which can be a polymer matrix of the above polymeric solid electrolyte. Further, there are demands on the development of a novel compound which can be a starting monomer capable of forming the above polymer.

OBJECT OF THE INVENTION

The present invention has been made in view of the above state of prior art. Thus, an object of the present invention is to provide a novel acrylic ester, allyl ether and allyl carbonate which can be starting monomers suitable for forming desired polymers. Another object of the present invention is to provide an acrylic ester polymer, allyl ether polymer and allyl carbonate polymer which can be polymer matrixes suitable for use in polymeric solid electrolytes. A further object of the present invention is to provide a polymeric solid electrolyte which exhibits high ionic conductivity and is chemically stable.

DISCLOSURE OF THE INVENTION

The first novel acrylic ester of the present invention is represented by the general formula (I):

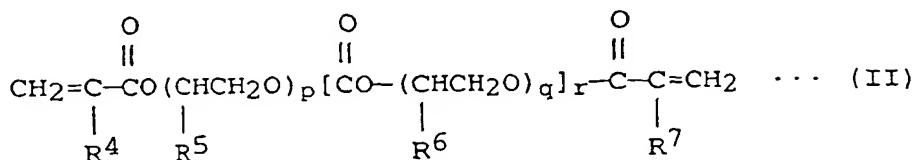


wherein

R¹ and R² may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; R³ represents an alkyl group having 1 to 4 carbon atoms; and n is an integer of 1 to

100.

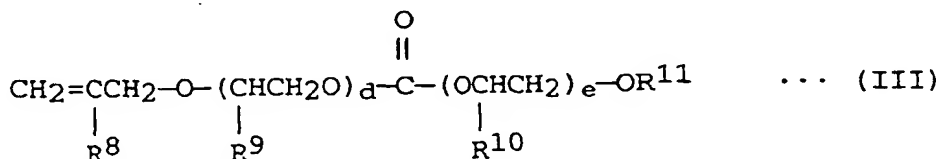
The second novel acrylic ester of the present invention is represented by the general formula (II):



wherein

R⁴ to R⁷ may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and p, q and r may be identical with or different from each other and each is an integer of 1 to 100.

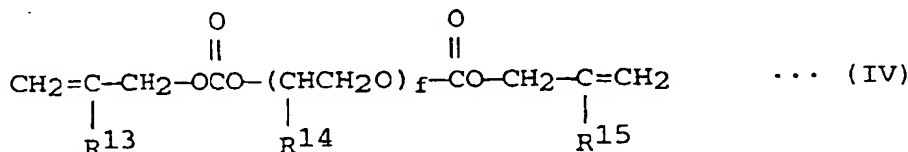
The novel allyl ether of the present invention is represented by the general formula (III):



wherein

R⁸, R⁹ and R¹⁰ may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; R¹¹ represents an alkyl group having 1 to 4 carbon atoms or CH₂CR¹²=CH₂ in which R¹² represents hydrogen atom or a methyl group; d is an integer of 0 to 100; and e is an integer of 1 to 100.

The novel allyl carbonate of the present invention is represented by the general formula (IV):



wherein

R¹³, R¹⁴ and R¹⁵ may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and f is an integer of 1 to 100.

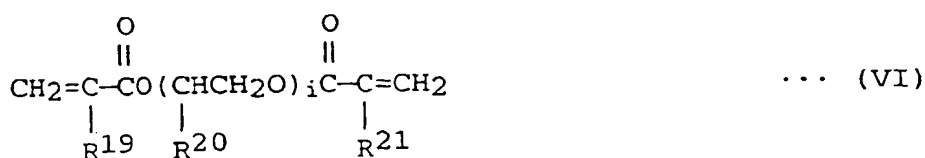
The first acrylic ester polymer of the present invention comprises structural units derived from at least one acrylic ester selected from a group of the acrylic esters represented by the above general formula (I).

Examples of the above first acrylic ester polymers include a homopolymer or copolymer of an acrylic ester selected from the group of the acrylic esters represented by the above general formula (I) and a copolymer of at least one acrylic ester selected from the group of the acrylic esters represented by the above general formula (I) and at least one compound selected from the group of the compounds represented by the above general formula (II) and the following general formulae (V) to (VIII):



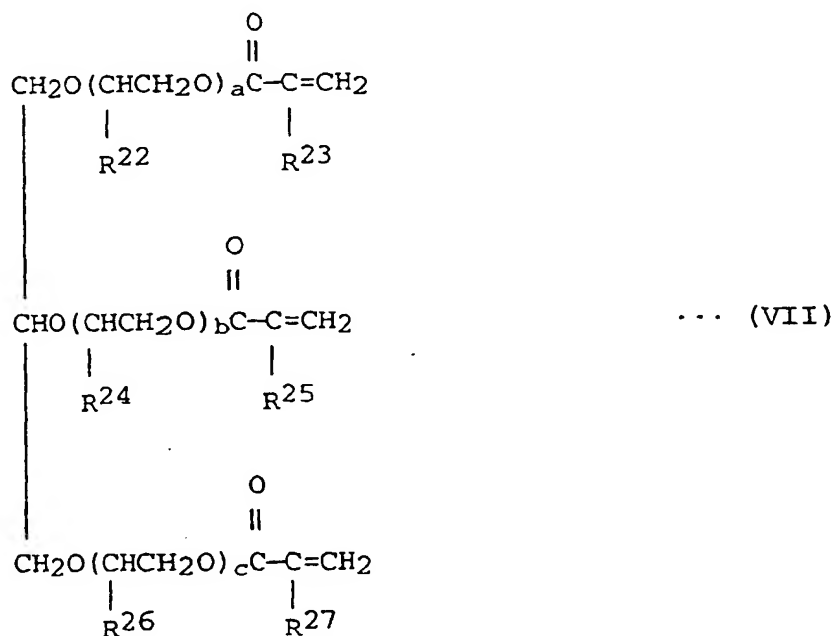
wherein

R¹⁶ and R¹⁷ may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; R¹⁸ represents an alkyl group having 1 to 4 carbon atoms; and m is an integer of 0 to 100.



wherein

R¹⁹, R²⁰ and R²¹ may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and i is an integer of 1 to 100.



wherein

R²² to R²⁷ may be identical with or different from each other and each represents hydrogen atom or an alkyl group

having 1 to 4 carbon atoms; and a, b and c may be identical with or different from each other and each are an integer of 0 to 100, and



wherein

k is an integer of 1 to 100.

The second acrylic ester polymer of the present invention comprises structural units derived from at least one acrylic ester selected from a group of the acrylic esters represented by the above general formula (VI).

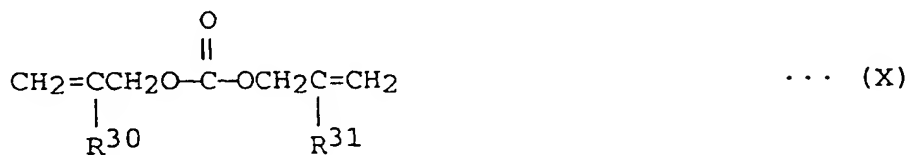
Examples of the above second acrylic ester polymers include a homopolymer or copolymer of an acrylic ester selected from the group of the acrylic esters represented by the above general formula (II) and a copolymer of at least one acrylic ester selected from the group of the acrylic esters represented by the above general formula (II) and at least one compound selected from a group of the compounds represented by the above general formulae (V) to (VIII). The allyl ether polymer of the present invention comprises structural units derived from at least one allyl ether selected from a group of the allyl ethers represented by the above general formula (III).

Examples of the above allyl ether polymers include a homopolymer or copolymer of an allyl ether selected from the group of the allyl ethers represented by the above general formula (III) and a copolymer of at least one allyl ether selected from the group of the allyl ethers represented by the above general formula (III) and at least one compound selected from a group of the compounds represented by the above general formulae (IV) and (VII) and the following general formula (IX) and (X):



wherein

R^{28} represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and R^{29} represents an alkyl group having 1 to 4 carbon atoms; and



wherein

each of R^{30} and R^{31} represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

The first allyl carbonate polymer of the present invention comprises structural units derived from at least one allyl carbonate selected from a group of the allyl carbonates represented by the above general formula (VI).

Examples of the above first allyl carbonate polymers include a homopolymer or copolymer of an allyl carbonate selected from a group of the allyl carbonates represented by the above general formula (IV) and a copolymer of at least one allyl carbonate selected from the group of the allyl carbonates represented by the above general formula (IV) and at least one compound selected from a group of the compounds represented by the above general formula (VII).

The second allyl carbonate polymer of the present invention comprises:

structural units derived from at least one compound selected from the group of the compounds represented by the above general formula (VII) and structural units derived from at least one compound selected from a group of the

compounds represented by the above general formula (IX).

The third allyl carbonate polymer of the present invention comprises:

structural units derived from at least one compound selected from the group of the compounds represented by the above general formula (VII) and structural units derived from at least one compound selected from a group of the compounds represented by the above general formula (X).

The polymeric solid electrolyte of the present invention comprises at least one member of the above acrylic ester polymers, allyl ether polymers and allyl carbonate polymers and a salt of a metal of Group Ia of the periodic table.

The polymeric solid electrolyte of the present invention comprises at least one member of the above acrylic ester polymers, allyl ether polymers and allyl carbonate polymers, a salt of a metal of Group Ia of the periodic table and a nonaqueous solvent.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is an NMR spectrum of methacrylic acid-2-hydroxyethyl methylcarbonate obtained in Example 1; Fig. 2 is an IR spectrum of methacrylic acid-2-hydroxyethyl methylcarbonate obtained in Example 1; Fig. 3 is an NMR spectrum of methacrylic acid-2-hydroxyethoxyethyl methylcarbonate obtained in Example 2; Fig. 4 is an IR spectrum of methacrylic acid-2-hydroxyethoxyethyl methylcarbonate obtained in Example 2; Fig. 5 is an IR spectrum of a copolymer of methacrylic acid-2-hydroxyethyl methylcarbonate and diethylene glycol dimethacrylate obtained in Example 7; Fig. 6 is an NMR spectrum of di-2-methacryloxy ethylcarbonate obtained in Example 26; Fig. 7 is an IR spectrum of di-2-methacryloxy ethylcarbonate obtained in Example 26; Fig. 8 is an IR spectrum of a copolymer of di-2-methacryloxy ethylcarbonate and diethylene glycol dimethacrylate obtained in Example 29; Fig. 9 is an NMR spectrum of 2-methoxyethoxyethoxyethyl allyl carbonate obtained in Example 44; Fig. 10 is an IR spectrum of 2-methoxyethoxyethoxyethyl allyl carbonate obtained in Example 44; Fig. 11 is an NMR spectrum of methoxyethyl allyloxyethyl carbonate obtained in Example 45; Fig. 12 is an IR spectrum of methoxyethyl allyloxyethyl carbonate obtained in Example 45; Fig. 13 is an IR spectrum of a copolymer of 2-methoxyethoxyethoxyethyl allyl carbonate and diallyl carbonate obtained in Example 48; Fig. 14 is an NMR spectrum of diethylene glycol diallyl dicarbonate obtained in Example 53; Fig. 15 is an IR spectrum of diethylene glycol diallyl dicarbonate and diallyl carbonate obtained in Example 57.

BEST MODE FOR CARRYING OUT THE INVENTION

The novel acrylic ester, novel allyl ether, novel allyl carbonate, acrylic ester polymer, allyl ether polymer, allyl carbonate polymer and polymeric solid electrolyte according to the present invention will be described in detail below.

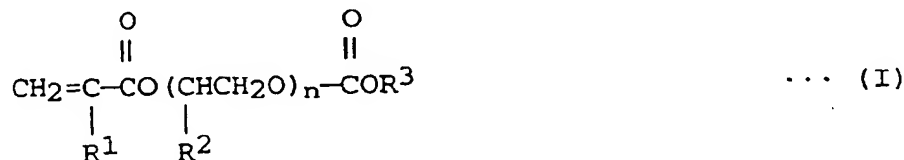
Herein, the meaning of the term "polymerization" is not limited to homopolymerization and may comprehend copolymerization. Likewise, the meaning of the term "polymer" is not limited to a homopolymer and may comprehend a copolymer.

[Novel acrylic ester]

First, the novel acrylic ester of the present invention will be described as follows.

First acrylic ester

The first novel acrylic ester of the present invention is represented by the general formula (I):



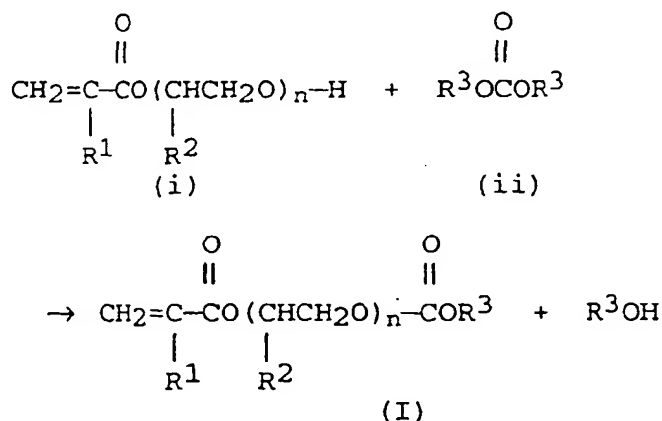
In the above general formula, R¹ and R² may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms, preferably, hydrogen atom or methyl group.

R³ represents an alkyl group having 1 to 4 carbon atoms, preferably, methyl group, ethyl group or t-butyl group.

n is an integer of 1 to 100, preferably 1 to 10.

Examples of the acrylic esters represented by the above general formula (I) include methacrylic acid-2-hydroxyethyl methylcarbonate, 2-(methacrylic acid-2-hydroxyethoxy) ethyl methylcarbonate, 2-hydroxy-methacrylic acid-ethyl ethylcarbonate, 2-hydroxyacrylethyl methylcarbonate and 2-(acryl-2-hydroxyethoxy)ethyl methylcarbonate.

The acrylic ester represented by the above general formula (I) can be synthesized by, for example, reacting the compound of the general formula (i) given below with the compound of the general formula (ii) given below in the following manner:



wherein

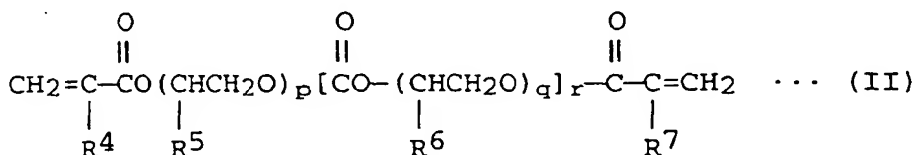
R¹, R², R³ and n have the same meaning as defined with respect to the general formula (I).

In the above synthetic process, the compound represented by the general formula (ii) is used in an amount of 0.5 to 5 mol based on 1 mol of the compound represented by the general formula (i). This reaction can be performed in the presence of a catalyst such as K₂CO₃, Na₂CO₃, Li₂CO₃ or NaOCH₃. This catalyst is used in an amount of 1 × 10⁻⁵ to 1 × 10⁻² mol based on 1 mol of the compound represented by the general formula (i).

The reaction between the compound represented by the general formula (i) and the compound represented by the general formula (ii) is generally conducted under reflux under agitation with removing formed alcohol. The reaction temperature generally ranges from 40 to 140°C and the reaction time generally ranges from 2 to 60 hrs.

Second acrylic ester

The second acrylic ester of the present invention is represented by the general formula (II):

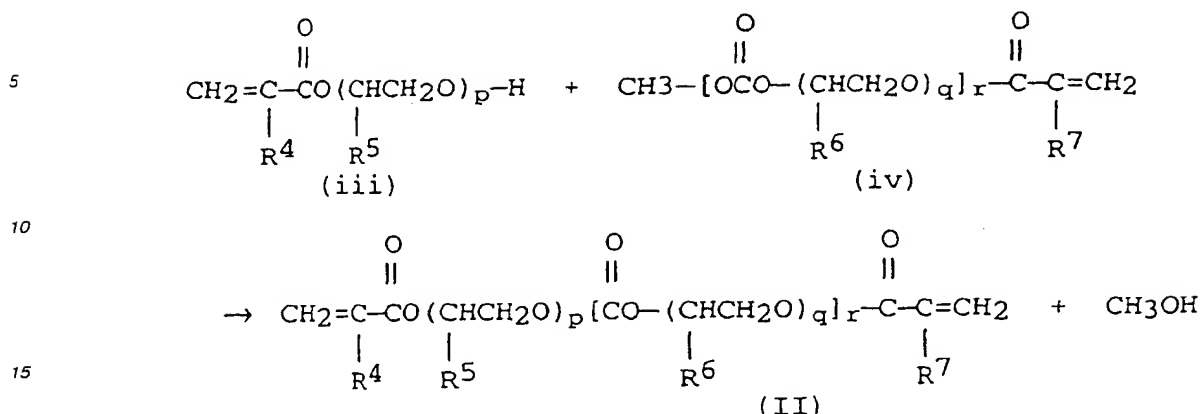


In the above general formula, R⁴ to R⁷ may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms, preferably hydrogen atom or methyl group. p, q and r may be identical with or different from each other and each is an integer of 1 to 100, preferably 1 to 10.

Examples of the acrylic esters represented by the above general formula (II) include di(2-methacryloxyethyl) carbonate, di(2-acryloxyethyl) carbonate, ethylene glycol di(2-methacryloxyethyl) carbonate, di(2-methacryloxy-2-methyl-ethyl) carbonate and diethylene glycol di(2-methacryloxyethyl) carbonate.

The compound represented by the above general formula (II) can be synthesized by, for example, reacting the compound of the general formula (iii) given below with the compound of the general formula (iv) given below in the following

manner:



wherein

R^4 , R^5 , R^6 , R^7 , p , q and r have the same meaning as defined with respect to the general formula (II).

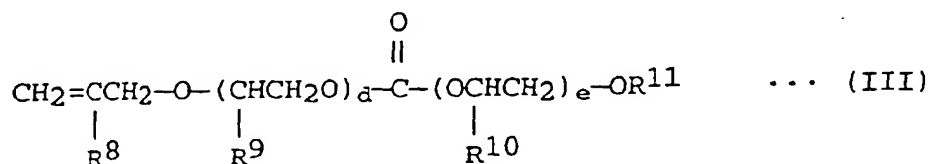
In the above synthetic process, the compound represented by the general formula (iv) is used in an amount of 0.3 to 2.0 mol based on 1 mol of the compound represented by the general formula (iii). This reaction can be performed in the presence of a catalyst such as K_2CO_3 , Na_2CO_3 , Li_2CO_3 or NaOCH_3 . This catalyst is used in an amount of 10^{-5} to 10^{-2} mol based on 1 mol of the compound represented by the general formula (iii).

The reaction between the compound represented by the general formula (iii) and the compound represented by the general formula (iv) is generally conducted under reflux under agitation with removing formed alcohol. The reaction temperature generally ranges from 40 to 140°C, preferably, 40 to 100°C and the reaction time generally ranges from 2 to 60 hrs.

The first and second acrylic esters of the present invention can be used as, for example, starting monomers for use in the production of an acrylic ester polymer. The polymeric solid electrolyte comprising, as a polymer matrix, the acrylic ester polymer having structural units derived from each of the first and second acrylic esters of the present invention exhibits high ionic conductivity and is chemically stable.

[Novel allyl ether]

The novel allyl ether of the present invention is represented by the general formula (III):



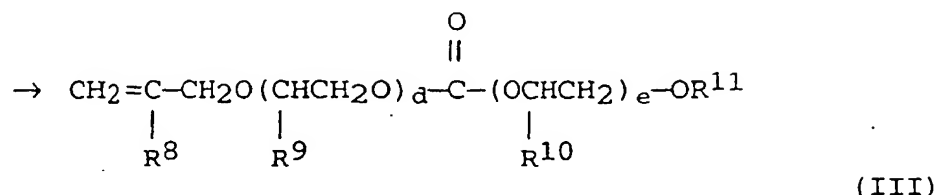
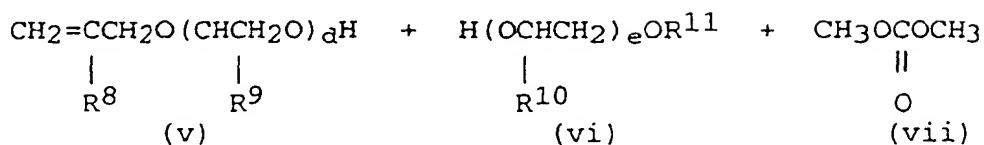
wherein

R^8 , R^9 and R^{10} may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; R^{11} represents an alkyl group having 1 to 4 carbon atoms or $\text{CH}_2\text{CR}^{12}=\text{CH}_2$ in which R^{12} represents hydrogen atom or methyl group; d is an integer of 0 to 100; and e is an integer of 1 to 100. d is preferred to be an integer of 0 to 10 and e is preferred to be an integer of 1 to 10.

Examples of the above allyl ethers include 2-methoxyethyl allyl carbonate, 2-methoxypropyl allyl carbonate, 2-ethoxyethyl allyl carbonate, 2-methoxyethyl methallyl carbonate, 2-(2-methoxyethoxy)ethyl allyl carbonate, di(2-allyloxyethyl) carbonate, di[2-(2-allyloxyethoxy)ethyl]carbonate and 2-(2-allyloxyethoxy)ethyl 2-allyloxyethyl carbonate.

The allyl ether represented by the above general formula (III) can be synthesized from, for example, the compounds

of the general formulae (v) to (vii) given below in the following manner:



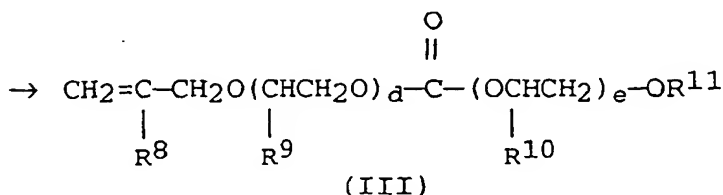
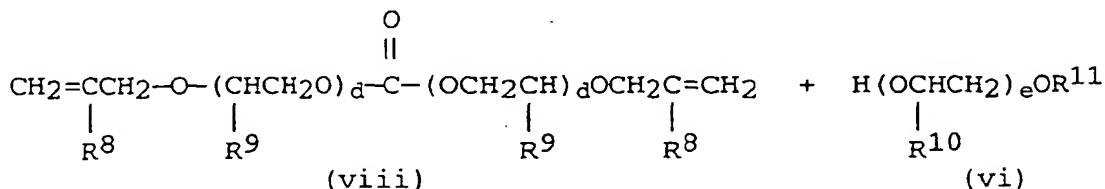
wherein

R^8 , R^9 , d and e have the same meaning as defined with respect to the general formula (III).

In the above synthesis using the compounds (v), (vi) and (vii), each of the compounds represented by the general formulae (v) and (vi) is used in an amount of 0.2 to 1.0 mol based on 1 mol of dimethyl carbonate (vii). This reaction can be performed in the presence of a catalyst such as LiOCH_3 , Li_2CO_3 , K_2CO_3 or Na_2CO_3 . This catalyst is used in an amount of 1×10^{-5} to 1×10^{-2} mol based on 1 mol of the compound represented by the general formula (v).

The above synthesis is generally conducted under reflux under agitation with removing formed alcohol. The reaction temperature generally ranges from 40 to 140°C and the reaction time generally ranges from 2 to 60 hr.

Further, the allyl ether represented by the above general formula (III) can be synthesized from the compound represented by the above general formula (vi) and the compound represented by the general formula (viii) given below in the following manner:



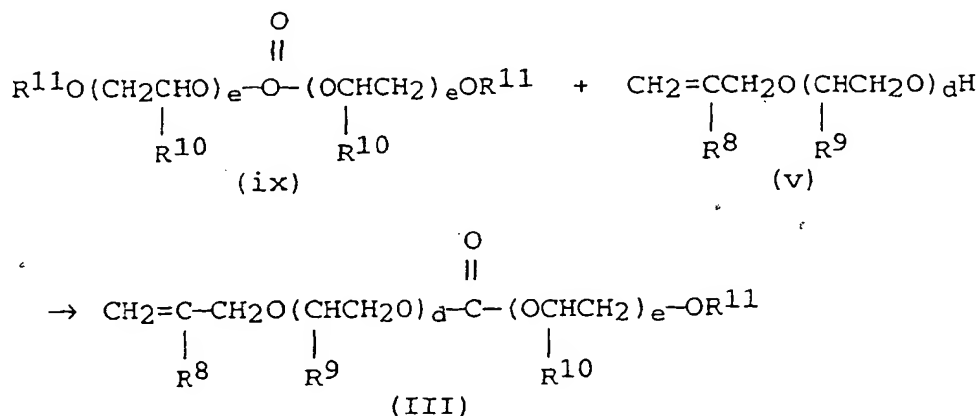
wherein

R^8 , R^9 and d have the same meaning as defined with respect to the general formula (III).

In the above synthesis using the compounds (viii) and (vi), the compound represented by the general formula (vi) is used in an amount of 0.5 to 2.0 mol based on 1 mol of the compound represented by the general formula (viii). This reaction can be performed in the presence of a catalyst such as LiOCH_3 , Li_2CO_3 , K_2CO_3 or Na_2CO_3 . This catalyst is used in an amount of 1×10^{-5} to 1×10^{-2} mol based on 1 mol of the compound represented by the general formula (viii). The reaction is generally conducted under reflux under agitation. The reaction temperature generally ranges from 40 to 140°C and the reaction time generally ranges from 2 to 60 hr.

Still further, the allyl ether represented by the above general formula (III) can be synthesized from the compound

represented by the above general formula (v) and the compound represented by the general formula (ix) given below in the following manner:



wherein

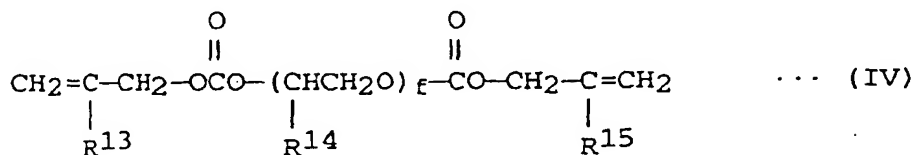
R^{10} , R^{11} and e have the same meaning as defined with respect to the general formula (III).

In the above synthesis using the compounds (v) and (ix), the compound represented by the general formula (ix) is used in an amount of 0.5 to 2.0 mol based on 1 mol of the compound represented by the general formula (v). This reaction can be performed in the presence of a catalyst such as LiOCH_3 , Li_2CO_3 , K_2CO_3 or Na_2CO_3 . This catalyst is used in an amount of 1×10^{-5} to 1×10^{-2} mol based on 1 mol of the compound represented by the general formula (v). The reaction is generally conducted under reflux under agitation. The reaction temperature generally ranges from 40 to 140°C and the reaction time generally ranges from 2 to 60 hr.

The allyl ether of the present invention can be used as, for example, a starting monomer for use in the production of an allyl ether polymer. The polymeric solid electrolyte comprising, as a polymer matrix, the allyl ether polymer having structural units derived from the allyl ether of the present invention exhibits high ionic conductivity and is chemically stable.

[Novel allyl carbonate]

The novel allyl carbonate of the present invention is represented by the general formula (IV):

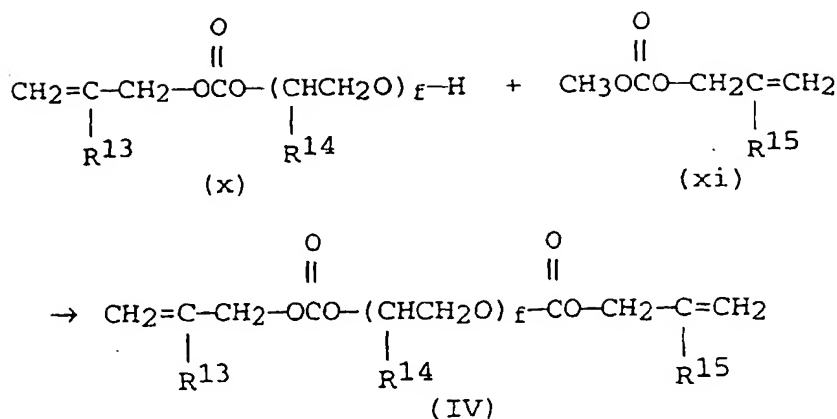


wherein

R^{13} , R^{14} and R^{15} may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and f is an integer of 0 to 100, preferably, 0 to 10.

Examples of the above allyl carbonates include ethylene glycol diallyl dicarbonate, diethylene glycol diallyl dicarbonate, diethylene glycol dimethallyl dicarbonate and triethylene glycol diallyl dicarbonate.

The allyl carbonate represented by the above general formula (IV) can be synthesized from, for example, the compound represented by the general formula (x) given below and the compound represented by the general formula (xi) given below in the following manner:



wherein

R^{13} to R^{15} and f have the same meaning as defined with respect to the general formula (IV).

In the above synthetic process, the compound represented by the general formula (xi) is used in an amount of 0.3 to 2.0 mol based on 1 mol of the compound represented by the general formula (x). This reaction can be performed in the presence of a catalyst such as K_2CO_3 , Na_2CO_3 , Li_2CO_3 or NaOCH_3 . This catalyst is used in an amount of 1×10^{-5} to 1×10^{-2} mol based on 1 mol of the compound represented by the general formula (x).

The reaction between the compound represented by the general formula (x) and the compound represented by the general formula (xi) is generally conducted under reflux under agitation with removing formed alcohol. The reaction temperature generally ranges from 40 to 140°C and the reaction time generally ranges from 2 to 60 hr.

The allyl carbonate of the present invention can be used as, for example, a starting monomer for use in the production of an allyl carbonate polymer. The polymeric solid electrolyte comprising, as a polymer matrix, the allyl carbonate polymer having structural units derived from the allyl carbonate of the present invention exhibits high ionic conductivity and is chemically stable.

[Acrylic ester polymer]

First acrylic ester polymer

The first acrylic ester polymer of the present invention comprises structural units derived from at least one acrylic ester selected from the group of the acrylic esters represented by the above general formula (I).

Examples of such polymers include a homopolymer of an acrylic ester selected from among the acrylic esters represented by the above general formula (I), a copolymer of at least two acrylic esters selected from the group of the acrylic esters represented by the above general formula (I) and a copolymer of at least one acrylic ester selected from the group of the acrylic esters represented by the above general formula (I) and at least one compound selected from the group of the compounds represented by the above general formula (II) and the general formulae (V) to (VIII) given below.

First, the compound represented by the general formula (V) will be described.



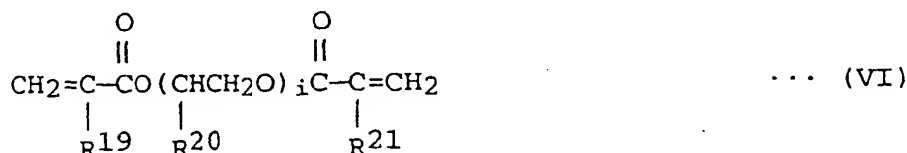
wherein

R^{16} and R^{17} may be identical with each other or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms, preferably hydrogen atom or methyl group.

R¹⁸ represents an alkyl group having 1 to 4 carbon atoms, preferably hydrogen atom or methyl group.
m is an integer of 0 to 100, preferably, 0 to 30.

Examples of the compounds represented by the above general formula (V) include methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate and 2-hydroxypropyl methacrylate.

Next, the compound represented by the general formula (VI) will be described.

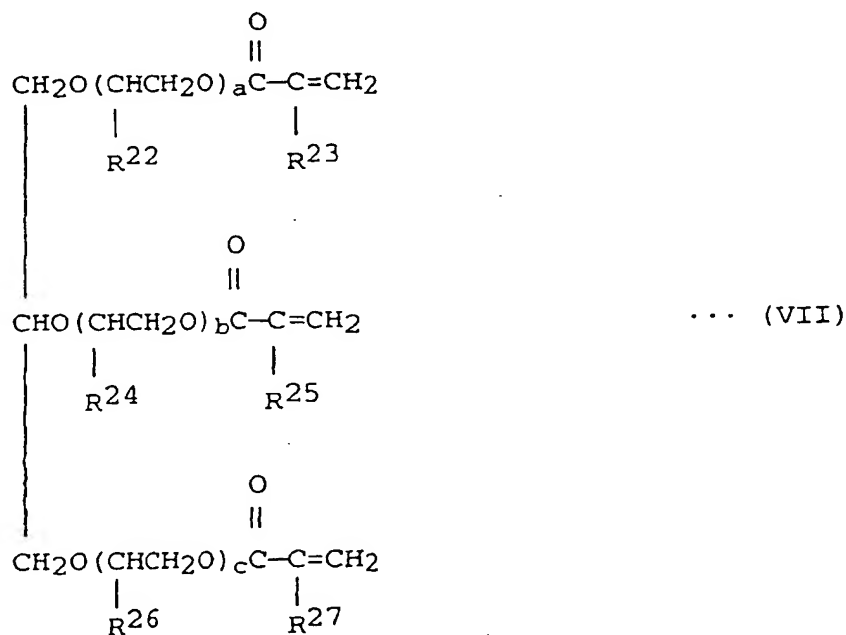


wherein

R¹⁹, R²⁰ and R²¹ may be identical with or different from each other and each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, preferably hydrogen atom or methyl group, and i is an integer of 1 to 100, preferably 1 to 10.

Examples of the compounds represented by the above general formula (VI) include diethylene glycol dimethacrylate, ethylene glycol dimethacrylate, diethylene glycol diacrylate, dipropylene glycol dimethacrylate and triethylene glycol dimethacrylate.

Now, the compound represented by the general formula (VII) will be described.



wherein

R²² to R²⁷ may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms, preferably hydrogen atom or methyl group, and a, b and c may be identical with or different from each other and each is an integer of 0 to 100, preferably 0 to 10.

Examples of the compounds represented by the above general formula (VII) include glycerol trimethacrylate, glycerol triacrylate, tri(2-methacryloxyethyl)glycerol and tri(2-acryloxyethyl)glycerol.

Finally, the compound represented by the general formula (VIII) will be described. The compound represented by the general formula (VIII) is polyethylene oxide.



wherein

k is an integer of 1 to 100, preferably 1 to 20.

This polyethylene oxide undergoes an ester exchange reaction with the acrylic ester represented by the above general formula (I).

The polymer of at least one acrylic ester selected from the group of the acrylic esters represented by the above general formula (I) which is a preferred embodiment of the present invention generally has a molecular weight ranging from 2×10^3 to 1×10^8 , preferably from 1×10^4 to 1×10^7 .

Although the proportion of structural units derived from two or more acrylic esters is not particularly limited in the copolymer of at least two acrylic esters selected from the group of the acrylic esters represented by the above general formula (I), it is preferred that the ratio of structural units derived from one acrylic ester range from 40 to 95 mol%.

The copolymer of an acrylic ester selected from the group of the acrylic esters represented by the above general formula (I) and at least one compound selected from the group of the compounds represented by the above general formula (II) and general formulae (V) to (VIII), which is another preferred embodiment of the present invention, generally has a molecular weight ranging from 2×10^3 to 1×10^8 , preferably from 1×10^4 to 1×10^7 . The molar ratio of structural units derived from the acrylic ester of the above general formula (I) to structural units derived from the compound selected from the group of the compounds of the above general formulae (II) and (V) to (VIII) generally ranges from 5:95 to 100:0, preferably from 5:95 to 95:5 and, still preferably from 10:90 to 90:10.

The molar ratio of structural units derived from the acrylic ester of the above general formula (I) to structural units derived from the compound selected from the group of the compounds of the above general formulae (II) and (V) to (VIII) is regulated within the above range in conformity with the desired physical and chemical properties of the copolymer.

When the molar ratio of structural units derived from the acrylic ester of the above general formula (I) to structural units derived from the compound selected from the group of the compounds of the above general formulae (II) and (V) to (VIII) falls outside the above range, problems may be encountered such that the ionic conductivity is lowered, and a viscosity and elasticity of the polymer are lowered, and the tensile strength is poor.

The first acrylic ester polymer of the present invention can be produced by customary methods. For example, it can easily be produced by polymerizing either at least one member selected from the group of the acrylic esters represented by the above general formula (I) or at least one member selected from the group of the acrylic esters represented by the above general formula (I) together with at least one compound selected from the group of the compounds represented by the above general formulae (II) and (V) to (VIII) according to the radical polymerization or photopolymerization technique.

The first acrylic ester polymer of the present invention may contain structural units other than the structural units derived from the monomers represented by the above general formulae (I), (II) and (V) to (VIII) in an amount of, for example, up to 20 mol%.

Second acrylic ester polymer

The second acrylic ester polymer of the present invention comprises structural units derived from at least one acrylic ester selected from the group of the acrylic esters represented by the above general formula (II).

Examples of such polymers include a homopolymer of an acrylic ester selected from the group of the acrylic esters represented by the above general formula (II), a copolymer of at least two acrylic esters selected from the group of the acrylic esters represented by the above general formula (II) and a copolymer of at least one acrylic ester selected from the group of the acrylic esters represented by the above general formula (II) and at least one compound selected from the group of the compounds represented by the above general formulae (V) to (VIII).

The polymer of at least one acrylic ester selected from the group of the acrylic esters represented by the above general formula (II) which is one of preferred embodiments of the present invention generally has a molecular weight ranging from 2×10^3 to 1×10^8 , preferably from 1×10^4 to 1×10^7 .

Although the proportion of structural units derived from two or more acrylic esters is not particularly limited in the copolymer of at least two acrylic esters selected from the group of the acrylic esters represented by the above general formula (II), it is preferred that the ratio of structural units derived from one acrylic ester range from 40 to 95 mol%.

The copolymer of an acrylic ester selected from the group of the acrylic esters represented by the above general formula (II) and at least one compound selected from the group of the compounds represented by the above general

formulae (V) to (VIII), which is another preferred embodiment of the present invention, generally has a molecular weight ranging from 2×10^3 to 1×10^8 , preferably from 1×10^4 to 1×10^7 . The molar ratio of structural units derived from the acrylic ester of the above general formula (II) to structural units derived from the compound selected from the group of the compounds of the above general formulae (V) to (VIII) generally ranges from 5:95 to 100:0, preferably from 5:95 to 95:5 and, still preferably from 10:90 to 90:10.

The molar ratio of structural units derived from the acrylic ester of the above general formula (II) to structural units derived from the compound selected from the group of the compounds of the above general formulae (V) to (VIII) is regulated within the above range in conformity with the desired physical and chemical properties of the copolymer.

When the molar ratio of structural units derived from the acrylic ester of the above general formula (II) to structural units derived from the compound selected from the group of the compounds of the above general formulae (V) to (VIII) falls outside the above range, problems may be encountered such that the ionic conductivity is lowered, and a viscosity and elasticity of the polymer are lowered, and the tensile strength is poor.

The second acrylic ester polymer of the present invention can be produced by customary methods. For example, it can easily be produced by polymerizing either at least one member selected from the group of the acrylic esters represented by the above general formula (II) or at least one member selected from the group of the acrylic esters represented by the above general formula (II) together with at least one compound selected from the group of the compounds represented by the above general formulae (V) to (VIII) according to the radical polymerization or photopolymerization technique.

The second acrylic ester polymer of the present invention may contain structural units other than the structural units derived from the monomers represented by the above general formulae (II) and (V) to (VIII) in an amount of, for example, up to 20 mol%.

[Allyl ether polymer]

The allyl ether polymer of the present invention comprises structural units derived from at least one allyl ether selected from the group of the allyl ethers represented by the above general formula (III).

Examples of the above allyl ether polymers include a homopolymer of an allyl ether selected from the group of the allyl ethers represented by the above general formula (III), a copolymer of at least two allyl ethers selected from the group of the allyl ethers represented by the above general formula (III) and a copolymer of at least one allyl ether selected from the group of the allyl ethers of represented by the above general formula (III) and at least one compound selected from the group of the compounds represented by the above general formulae (IV) and (VII) and the following general formulae (IX) and (X).

First, the compound represented by the general formula (IX) will be described.

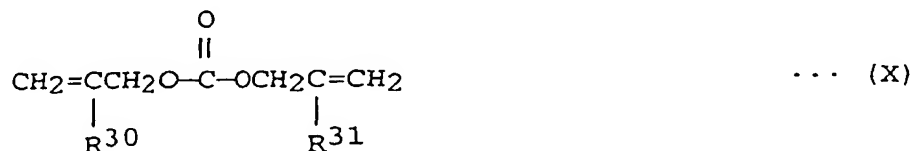


wherein

R^{28} represents an alkyl group having 1 to 4 carbon atoms; and R^{29} represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

Examples of the above compounds represented by the general formula (IX) include methyl allyl carbonate, ethyl allyl carbonate, methyl methallyl carbonate, methyl ethallyl carbonate, propyl allyl carbonate and butyl allyl carbonate.

The compound represented by the general formula (X) is as follows:



wherein

each of R^{30} and R^{31} represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms. Examples of the above compounds represented by the general formula (IX) include diallyl carbonate, dimethallyl carbonate, diethallyl carbonate, allyl methallyl carbonate and allyl ethallyl carbonate.

The polymer of at least one allyl ether selected from the group of the allyl ethers represented by the above general formula (III) which is one of preferred embodiments of the present invention generally has a molecular weight ranging from 1×10^3 to 1×10^7 , preferably from 1×10^4 to 1×10^6 .

Although the proportion of structural units derived from two or more allyl ethers is not particularly limited in the copolymer of at least two allyl ethers selected from the group of the allyl ethers represented by the above general formula (III), it is preferred that the ratio of structural units derived from one allyl ether ranges from 30 to 95 mol%.

The copolymer of at least one allyl ether selected from the group of the allyl ethers represented by the above general formula (III) and at least one compound selected from the group of the compounds represented by the above general formulae (IV), (VII), (IX) and (X), which is another preferred embodiment of the present invention, generally has a molecular weight ranging from 1×10^3 to 1×10^7 , preferably from 1×10^4 to 1×10^6 . The molar ratio of structural units derived from the allyl ether of the above general formula (III) to structural units derived from the compound selected from the group of those of the above general formulae (IV), (VII), (IX) and (X) generally ranges from 5:95 to 95:5, preferably from 10:90 to 90:10.

The molar ratio of structural units derived from the allyl ether of the above general formula (III) to structural units derived from the compound selected from the group of those of the above general formulae (IV), (VII), (IX) and (X) is regulated within the above range in conformity with the desired physical and chemical properties of the copolymer.

When the molar ratio of structural units derived from the allyl ether of the above general formula (III) to structural units derived from the compound selected from the group of the compounds of the above general formulae (IV), (VII), (IX) and (X) falls outside the above range, problems may be encountered such that the ionic conductivity is lowered, and a viscosity and elasticity of the polymer are lowered, and the tensile strength is poor.

The above allyl ether polymer can be produced by customary methods. For example, it can easily be produced by polymerizing either at least one member selected from the group of the allyl ethers represented by the above general formula (III) or at least one member selected from the group of the allyl ethers represented by the above general formula (III) together with at least one compound selected from the group of the compounds represented by the above general formulae (IV), (VII), (IX) and (X) according to the radical polymerization or photopolymerization technique.

The allyl ether polymer of the present invention may contain structural units other than the structural units derived from the monomers represented by the above general formulae (III), (IV), (VII), (IX) and (X) in an amount of, for example, up to 20 mol%.

[Allyl carbonate polymer]

First allyl carbonate polymer

The first allyl carbonate polymer of the present invention comprises structural units derived from at least one allyl carbonate selected from the group of the allyl carbonates represented by the above general formula (IV).

Examples of such polymers include a homopolymer of an allyl carbonate selected from the group of the allyl carbonates represented by the above general formula (IV), a copolymer of at least two allyl carbonates selected from the group of the allyl carbonates represented by the above general formula (IV) and a copolymer of at least one allyl carbonate selected from the group of the allyl carbonates represented by the above general formula (IV) and at least one compound selected from the group of the compounds represented by the above general formula (VII).

The polymer of at least one allyl carbonate selected from the group of the allyl carbonates represented by the above general formula (IV) which is one of preferred embodiments of the present invention generally has a molecular weight ranging from 1×10^3 to 1×10^7 , preferably from 1×10^4 to 1×10^6 .

Although the proportion of structural units derived from two or more allyl carbonates is not particularly limited in the copolymer of at least two allyl carbonates selected from the group of the allyl carbonates represented by the above general formula (IV), it is preferred that the ratio of structural units derived from one allyl carbonate ranges from 30 to 95 mol%.

The copolymer of at least one allyl carbonate selected from the group of the allyl carbonates represented by the above general formula (IV) and at least one compound selected from the group of the compounds represented by the above general formula (VII), which is another preferred embodiment of the present invention, generally has a molecular weight ranging from 1×10^3 to 1×10^7 , preferably from 1×10^4 to 1×10^6 . The molar ratio of structural units derived from the allyl carbonate of the above general formula (IV) to structural units derived from the compound of the above general formula (VII) generally ranges from 5:95 to 100:0, preferably from 10:90 to 90:10.

The molar ratio of structural units derived from the allyl carbonate of the above general formula (IV) to structural units derived from the compound of the above general formula (VII) is regulated within the above range in conformity

with the desired physical and chemical properties of the copolymer.

When the molar ratio of structural units derived from the allyl carbonate of the above general formula (IV) to structural units derived from the compound of the above general formula (VII) falls outside the above range, problems may be encountered such that the ionic conductivity is lowered, and a viscosity and elasticity of the polymer are lowered, and the tensile strength is poor.

The above allyl carbonate polymer can be produced by customary methods. For example, it can easily be produced by polymerizing either at least one member selected from the group of the allyl carbonates represented by the above general formula (IV) or at least one member selected from the group of the allyl carbonates represented by the above general formula (IV) together with at least one compound selected from the group of the compounds represented by the above general formula (VII) according to the radical polymerization or photopolymerization technique.

The first allyl carbonate polymer of the present invention may contain structural units other than the structural units derived from the monomers represented by the above general formulae (IV) and (VII) in an amount of, for example, up to 20 mol%.

Second allyl carbonate polymer

The second allyl carbonate polymer of the present invention comprises:

structural units derived from at least one compound selected from the group of the compounds represented by the above general formula (IX) and structural units derived from at least one compound selected from the group of the compounds represented by the above general formula (VII).

The allyl carbonate polymer of the present invention generally has a molecular weight ranging from 2×10^3 to 1×10^8 , preferably from 1×10^4 to 1×10^7 . The molar ratio of structural units derived from the compound of the above general formula (IX) to structural units derived from the compound of the above general formula (VII) generally ranges from 10:90 to 99:1, preferably from 30:70 to 97:3 and still preferably from 50:50 to 95:5.

The molar ratio of structural units derived from the compound of the above general formula (IX) to structural units derived from the compound of the above general formula (VII) is regulated within the above range in conformity with the desired physical and chemical properties of the copolymer.

When the molar ratio of structural units derived from the compound of the above general formula (IX) to structural units derived from the compound of the above general formula (VII) falls outside the above range, problems may be encountered such that the ionic conductivity is lowered, and a viscosity and elasticity of the polymer are lowered, and the tensile strength is poor.

The above allyl carbonate copolymer can be produced by customary methods. For example, it can easily be produced by polymerizing at least one compound selected from the group of the compounds represented by the above general formula (IX) together with at least one compound selected from the group of the compounds represented by the above general formula (VII) according to the radical polymerization or photopolymerization technique.

The second allyl carbonate polymer of the present invention may contain structural units other than the structural units derived from the compound of the above general formula (IX) and structural units derived from the compound of the above general formula (VII) in an amount such that the properties of the copolymer of the present invention are not deteriorated, for example, up to 20 mol%.

Third allyl carbonate polymer

The third allyl carbonate polymer of the present invention comprises:

structural units derived from at least one compound selected from the group of the compounds represented by the above general formula (X) and structural units derived from at least one compound selected from the group of the compounds represented by the above general formula (VII).

The third allyl carbonate polymer of the present invention generally has a molecular weight ranging from 2×10^3 to 1×10^8 , preferably from 1×10^4 to 1×10^7 . The molar ratio of structural units derived from the compound of the above general formula (X) to structural units derived from the compound of the above general formula (VII) generally ranges from 10:90 to 99:1, preferably from 30:70 to 97:3 and still preferably from 50:50 to 95:5.

The molar ratio of structural units derived from the compound of the above general formula (X) to structural units derived from the compound of the above general formula (VII) is regulated within the above range in conformity with the desired physical and chemical properties of the copolymer.

When the molar ratio of structural units derived from the compound of the above general formula (X) to structural units derived from the compound of the above general formula (VII) falls outside the above range, problems may be

encountered such that the ionic conductivity is lowered, and a viscosity and elasticity of the polymer are lowered, and the tensile strength is poor.

The above allyl carbonate copolymer can be produced by customary methods. For example, it can easily be produced by polymerizing at least one compound selected from the group of the compounds represented by the above general formula (X) together with at least one compound selected from the group of the compounds represented by the above general formula (VII) according to the radical polymerization or photopolymerization technique.

The third allyl carbonate polymer of the present invention may contain structural units other than the structural units derived from the compound of the above general formula (X) and structural units derived from the compound of the above general formula (VII) in an amount such that the properties of the copolymer of the present invention are not deteriorated, for example, up to 20 mol%.

[Polymeric solid electrolyte]

The polymeric solid electrolyte of the present invention comprises at least one polymer selected from the group of the above acrylic ester polymers, allyl ether polymers and allyl carbonate polymers and a salt of a metal of Group Ia of the periodic table, optionally together with a nonaqueous solvent.

It is preferred that the above salt of a metal of Group Ia of the periodic table is selected from the group consisting of LiBr, LiI, LiSCN, LiClO₄, LiBF₄, LiAsF₆, LiPF₆, LiCF₃SO₃, LiAlCl₄, LiN(CF₃SO₂)₂, LiC(CF₃SO₂)₃, NaBr, NaSCN, NaClO₄, KSCN and KClO₄. Of these, LiClO₄, LiBF₄, LiPF₆, LiAsF₆, LiCF₃SO₃, LiN(CF₃SO₂)₂ and LiC(CF₃SO₂)₃ are especially preferred. The above salts can be used singly or in combination of two or more kinds.

The salt of a metal of Group Ia of the periodic table is preferably contained in the polymeric solid electrolyte of the present invention in an amount of 5 to 50% by weight, especially 10 to 40% by weight based on the total weight of the polymeric solid electrolyte.

When the proportion of the salt of a metal of Group Ia of the periodic table to at least one polymer selected from the group of the above acrylic ester polymers, allyl ether polymers and allyl carbonate polymers falls outside the above range, problems may be encountered such that the ionic conductivity is lowered, and a viscosity and elasticity of the polymer are lowered, and the tensile strength is poor.

The polymeric solid electrolyte of the present invention can be produced by customary methods.

The polymeric solid electrolyte is generally used in the form of a film, so that the employment of the following methods is preferred.

1. Method comprising dissolving at least one polymer selected from the group of the above polymerized acrylic ester polymers, allyl ether polymers and allyl carbonate polymers and the Group Ia metal salt in a solvent or impregnating them with the solvent, and applying the resultant solution or mixture to a flat substrate by casting or coating, in which, optionally, the solvent is evaporated after the application. Although the solvent is not particularly limited as long as it can dissolve the polymer, the solvent can be selected from the group consisting of, for example, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, propylene carbonate, ethylene carbonate, γ -butyrolactone, dimethylformamide, dimethylacetamide, tetrahydrofuran, dimethyl sulfoxide, N-methylpyrrolidone and sulfolane.
2. Method comprising dissolving one or more compounds set forth below in a solvent in the presence of the Group Ia metal salt, applying the resultant solution to a flat substrate by casting or coating, and irradiating ultraviolet or radiation or heating to effect polymerization and curing the resulting polymer.

(1) at least one compound selected from the group of the compounds represented by the above general formulae (I) to (IV);

(2) at least one member selected from the group of the acrylic esters represented by the above general formula (I) and at least one compound selected from the group of the compounds represented by the above general formulae (II) and (V) to (VIII);

(3) at least one member selected from a group of the acrylic esters represented by the above general formula (II) and at least one compound selected from the group of the compounds represented by the above general formulae (V) to (VIII);

(4) at least one member selected from the group of the allyl ethers represented by the above general formula (III) and at least one compound selected from the group of the compounds represented by the above general formulae (IV), (VII), (IX) and (X);

(5) at least one member selected from the group of the allyl carbonates represented by the above general formula (IV) and at least one compound selected from the group of the compounds represented by the above general formula (VII);

(6) at least one member selected from the group of the compounds represented by the above general formula (IX) and at least one compound selected from the group of the compounds represented by the above general

formula (VII); and

(7) at least one member selected from the group of the compounds represented by the above general formula (X) and at least one compound selected from the group of the compounds represented by the above general formula (VII).

5

In this method, the solvent may be evaporated after the spread of the solution on the flat substrate. Examples of suitable solvents include methyl ethyl ketone, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, propylene carbonate, ethylene carbonate, γ -butyrolactone and dimethylformamide.

10 Further, a photosensitizer can be used in this method. Examples of suitable photosensitizers include benzophenone, acetophenone and 2,2-dimethoxy-2-phenylacetophenone.

3. Method comprising dissolving one or more compounds set forth in items (1) to (7) above in a solvent in the presence of the Group Ia metal salt and a polymerization initiator, applying the resultant solution to a flat substrate by casting or coating and heating the solution to effect polymerization and curing the resulting polymer. In this method, 15 the solvent may be evaporated after the spread of the solution on the flat substrate. The same solvents as set forth in the method 2 can be used in this method as well.

A gelled polymeric solid electrolyte can be produced by performing the polymerization without the evaporation of the solvent in the methods 2 and 3.

20 In the present invention, the polymeric solid electrolyte may be in the form of a bulk or a gel.

The gelled polymeric solid electrolyte of the present invention comprises a member selected from the group of the above acrylic ester polymers, allyl ether polymers and allyl carbonate polymers, a salt of a metal of Group Ia of the periodic table and a nonaqueous solvent.

Salts set forth hereinbefore can be used as the salt of a metal of Group Ia of the periodic table.

25 The nonaqueous solvent is, for example, methyl ethyl ketone, dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, propylene carbonate, ethylene carbonate, γ -butyrolactone or dimethylformamide. Of these, propylene carbonate and ethylene carbonate are preferred.

The content of a nonaqueous solvent is preferred to range from 0 to 600 parts by weight, especially from 5 to 300 parts by weight and still especially from 10 to 250 parts by weight based on 100 parts by weight of the acrylic ester polymer, allyl ether polymer and/or allyl carbonate polymer.

30 The polymeric solid electrolyte of the present invention exhibits high ionic conductivity and is electrochemically stable, so that it can be used in, for example, an electrochemical element such as a primary battery, a secondary battery, a capacitor or an electrochromic display and a medical actuator.

35 EFFECT OF THE INVENTION

Each of the novel acrylic ester, allyl ether and allyl carbonate according to the present invention can be a starting monomer capable of forming a polymer matrix for use in, for example, a polymeric solid electrolyte. The polymeric solid electrolyte comprising as a polymer matrix each of the acrylic ester polymer, allyl ether polymer and allyl carbonate polymer which have structural units derived from the acrylic ester, allyl ether and allyl carbonate according to the present invention, respectively, exhibits high ionic conductivity and is electrochemically stable.

Each of the acrylic ester polymer, allyl ether polymer and allyl carbonate polymer according to the present invention can be used, for example, as a polymer matrix in a polymeric solid electrolyte. The polymeric solid electrolyte comprising as a polymer matrix each of the acrylic ester polymer, allyl ether polymer and allyl carbonate polymer according to the present invention exhibits high ionic conductivity and is electrochemically stable.

45 The polymeric solid electrolyte of the present invention exhibits high ionic conductivity and is electrochemically stable, so that it can be used in, for example, an electrochemical element such as a primary battery, a secondary battery, a capacitor or an electrochromic display and a medical actuator.

50 EXAMPLE

The present invention will be illustrated below with reference to the following Examples, which in no way limit the scope of the invention.

55 The acrylic ester polymer, allyl ether polymer, allyl carbonate polymer and polymeric solid electrolyte were evaluated by the methods described later.

Example 1Synthesis of methacrylic acid-2-hydroxyethyl methylcarbonate

13.01 g (0.1 mol) of hydroxyethyl methacrylate, 27.00 g (0.3 mol) of dimethyl carbonate and 0.042 g (0.3 mmol) of potassium carbonate as a catalyst were charged into a 100 ml four-necked flask and reacted at 90°C for 8 hr under reflux under agitation with removing formed methanol. After the completion of the reaction, potassium carbonate was removed by the use of a silica gel column and distillation was performed, thereby obtaining methacrylic acid-2-hydroxyethyl methylcarbonate.

Identification of the obtained methacrylic acid-2-hydroxyethyl methylcarbonate was conducted by NMR and IR. NMR and IR spectra are shown in Figs. 1 and 2, respectively.

NMR (CDCl₃ solution, δ ppm): 1.95 (t, 3H, J=1.0 Hz, CH₃), 3.80 (s, 3H, CH₃), 4.38 (m, 4H, CH₂), 5.59 (t, 1H, J=1.5 Hz, CH), 6.14 (s, 1H, CH).

IR (neat, cm⁻¹): 2960 (C-H), 1755 (C=O), 1720 (C=O), 1640 (C=C), 1450, 1272, 1170, 1048, 1015, 935, 790.

Example 2Synthesis of methacrylic acid-2-hydroxyethoxyethyl methylcarbonate

86.1 g of methacrylic acid, 106.1 g of diethylene glycol, 0.3 g of hydroquinone, 1.5 ml of concentrated sulfuric acid and 500 ml of toluene were charged into a 1 lit. four-necked flask equipped with an agitator, a water separator and a thermometer and an esterification reaction was performed at 110°C under agitation with separating water. After the completion of the reaction for 3 hr, the resulting mixture was cooled to room temperature. The amount of formed water was 18 g.

The reaction mixture was concentrated with toluene removed and dissolved in a 1:1 (vol/vol) mixture of hexane and ether. The methacrylic acid as a raw material, sulfuric acid as a catalyst and desired diethylene glycol monomethacrylate were extracted with 10% aqueous sodium bicarbonate. The water layer was further extracted with ether, and the concentration was conducted, thereby obtaining 52 g of diethylene glycol monomethacrylate.

52 g (0.3 mol) of diethylene glycol monomethacrylate, 270 g (3 mol) of dimethyl carbonate and 0.13 g (0.9 mmol) of potassium carbonate as a catalyst were charged into a 500 ml four-necked flask and reacted at 90°C for 8 hr under reflux under agitation with removing formed methanol. After the completion of the reaction, potassium carbonate was removed by the use of a silica gel column and distillation was performed, thereby obtaining methacrylic acid-2-hydroxyethoxyethyl methylcarbonate.

Identification of the obtained methacrylic acid-2-hydroxyethoxyethyl methylcarbonate was conducted by NMR and IR. NMR and IR spectra are shown in Figs. 3 and 4, respectively.

NMR (CDCl₃ solution, δ ppm): 1.95 (t, 3H, J=1.3 Hz, CH₃), 3.75 (m, 4H, CH₂), 3.78 (s, 3H, CH₃), 4.30 (m, 4H, CH₂), 5.58 (t, 1H, J=1.5 Hz, CH), 6.70 (s, 1H, CH).

IR (neat, cm⁻¹): 2980 (C-H), 1750 (C=O), 1710 (C=O), 1640 (C=C), 1450, 1265, 1175, 1135, 1032, 952, 785.

Example 3Preparation of acrylic ester polymer

1.88 g (0.01 mol) of methacrylic acid-2-hydroxyethyl methylcarbonate produced in Example 1 was mixed with 41.6 μ l of Peroyl IPP50 (produced by Nippon Oil & Fats Co., Ltd.). The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a transparent solid. A polymerization was confirmed by the extinction of absorption at 1640 cm⁻¹ ascribed to C=C vibration in an IR spectrum of the solid.

Example 4Preparation of acrylic ester polymer

The same curing and confirmation of polymerization by IR spectrum as in Example 3 were executed using the methacrylic acid-2-hydroxyethoxyethyl methylcarbonate produced in Example 2.

Example 5Preparation of acrylic ester copolymer

0.94 g (0.005 mol) of methacrylic acid-2-hydroxyethyl methylcarbonate produced in Example 1, 1.16 g (0.005 mol) of methacrylic acid-2-hydroxyethoxyethyl methylcarbonate produced in Example 2 and 41.6 μ l of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a transparent solid. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the solid.

Example 6Preparation of methacrylic acid-2-hydroxyethyl methylcarbonate copolymer

0.94 g (0.005 mol) of methacrylic acid-2-hydroxyethyl methylcarbonate produced in Example 1, 0.94 g (0.005 mol) of methoxyethoxyethyl methacrylate and 41.6 μ l of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a transparent solid. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the solid.

Example 7

A copolymer was prepared in the same manner as in Example 6 except that diethylene glycol dimethacrylate was employed in place of methoxyethoxyethyl methacrylate. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the copolymer.

The obtained IR spectrum is shown in Fig. 5.

Example 8

A copolymer was prepared in the same manner as in Example 6 except that di-2-methacryloxyethyl carbonate was employed in place of methoxyethoxyethyl methacrylate.

Example 9Preparation of methacrylic acid-2-hydroxyethoxyethyl methylcarbonate copolymer

1.16 g (0.005 mol) of methacrylic acid-2-hydroxyethoxyethyl methylcarbonate produced in Example 2, 0.94 g (0.005 mol) of methoxyethoxyethyl methacrylate and 41.6 μ l of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a transparent solid. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the solid.

Example 10

A copolymer was prepared in the same manner as in Example 9 except that diethylene glycol dimethacrylate was employed in place of methoxyethoxyethyl methacrylate.

Example 11

A copolymer was prepared in the same manner as in Example 9 except that di-2-methacryloxyethyl carbonate was employed in place of methoxyethoxyethyl methacrylate.

Example 12Production of polymeric electrolyte and measurement of ionic conductivity

50% by weight of methacrylic acid-2-hydroxyethyl methylcarbonate produced in Example 1, 50% by weight of propylene carbonate, 2 mol%, based on the carbonate units, of Group Ia metal salt of the formula $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 1 mol%, based on the monomers, of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast

on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a thin-film polymeric solid electrolyte of about 1 mm in thickness composed of the acrylic ester polymer and the Group Ia metal salt. A polymerization was confirmed by the extinction of absorption at 1640 cm⁻¹ ascribed to C=C vibration in an IR spectrum of the electrolyte.

In the present invention, the thus obtained thin-film polymeric solid electrolyte was punched to thereby obtain a disc of 10 mmØ in diameter. This disc was interposed between electrodes and fitted in an impedance measuring holder, and the complex impedance thereof was measured by means of impedance analyzer HP4285A (measuring voltage: 10 mV) with controlling the temperature of the electrodes with the use of Peltier device. Thus, the ionic conductivity was analytically determined. The results are given in Table 1.

Example 13

A polymeric electrolyte was produced in the same manner as in Example 12 except that methacrylic acid-2-hydroxyethoxyethyl methylcarbonate produced in Example 2 was employed in place of methacrylic acid-2-hydroxyethyl methylcarbonate.

The ionic conductivity of the obtained polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 1.

Example 14

A polymeric electrolyte was produced in the same manner as in Example 12 except that a 5:5 (mol:mol) monomer mixture of methacrylic acid-2-hydroxyethyl methylcarbonate and methacrylic acid-2-hydroxyethoxyethyl methylcarbonate produced in Example 2 was employed in place of methacrylic acid-2-hydroxyethyl methylcarbonate.

The ionic conductivity of the obtained polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 1.

Example 15

70% by weight of a 5:5 (mol:mol) monomer mixture, of methacrylic acid-2-hydroxyethyl methylcarbonate produced in Example 1 and methoxyethoxyethyl methacrylate, 30% by weight of propylene carbonate, 2 mol%, based on the carbonate units, of Group Ia metal salt of the formula LiN(CF₃SO₂)₂ and 1 mol%, based on the monomers, of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt. A polymerization was confirmed by the extinction of absorption at 1640 cm⁻¹ ascribed to C=C vibration in an IR spectrum of the electrolyte.

The ionic conductivity of the obtained polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 1.

Example 16

A polymeric electrolyte was produced in the same manner as in Example 15 except that diethylene glycol dimethacrylate was employed in place of methoxyethoxyethyl methacrylate and that the monomer ratio of the mixture was changed to 9:1 (mol:mol).

The ionic conductivity of the obtained polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 1.

Example 17

A polymeric electrolyte was produced in the same manner as in Example 15 except that di-2-methacryloxyethyl carbonate was employed in place of methoxyethoxyethyl methacrylate and that the monomer ratio of the mixture was changed to 9:1 (mol:mol).

The ionic conductivity of the obtained polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 1.

Example 18

70% by weight of a 5:5 (mol:mol) monomer mixture of methacrylic acid-2-hydroxyethoxyethyl methylcarbonate produced in Example 2 and methoxyethoxyethyl methacrylate, 30% by weight of propylene carbonate, 2 mol%, based on the carbonate units, of Group Ia metal salt of the formula LiN(CF₃SO₂)₂ and 1 mol%, based on the monomers, of Peroyl

IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt. A polymerization was confirmed by the extinction of absorption at 1640 cm⁻¹ ascribed to C=C vibration in an IR spectrum of the electrolyte.

The ionic conductivity of the obtained polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 1.

Example 19

A polymeric electrolyte was produced in the same manner as in Example 18 except that diethylene glycol dimethacrylate was employed in place of methoxyethoxyethyl methacrylate and that the monomer ratio of the mixture was changed to 9:1 (mol:mol).

The ionic conductivity of the obtained polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 1.

Example 20

A polymeric electrolyte was produced in the same manner as in Example 18 except that di-2-methacryloxyethyl carbonate was employed in place of methoxyethoxyethyl methacrylate and that the monomer ratio of the mixture was changed to 9:1 (mol:mol).

The ionic conductivity of the obtained polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 1.

Table 1

Measurement of Ionic Conductivity	
Example	Conductivity (S/cm)
12	8.5×10^{-4}
13	1.9×10^{-3}
14	1.9×10^{-3}
15	7.5×10^{-5}
16	1.8×10^{-6}
17	1.1×10^{-5}
18	4.8×10^{-5}
19	3.9×10^{-5}
20	8.8×10^{-6}

Example 21

5.0 g of methacrylic acid-2-hydroxyethyl methylcarbonate produced in Example 1, 0.5 g of LiClO₄, 5.0 g of methyl ethyl ketone and 0.025 g of benzophenone were mixed together. The thus obtained homogeneous solution was cast on a glass plate in dry inert gas atmosphere and the methyl ethyl ketone was evaporated off. The resultant layer was irradiated with ultraviolet rays in dry inert gas atmosphere to thereby polymerize and cure the methacrylic acid-2-hydroxyethyl methylcarbonate. Thus, a polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt (LiClO₄) was obtained.

Example 22

A polymeric solid electrolyte was produced in the same manner as in Example 21 except that propylene carbonate was employed in place of methyl ethyl ketone and that the propylene carbonate was not evaporated off.

Example 23

5.0 g of methacrylic acid-2-hydroxyethyl methylcarbonate produced in Example 1, 0.5 g of LiBF₄, 5.0 g of methyl ethyl ketone and 0.025 g of benzoyl peroxide were mixed together. The thus obtained homogeneous solution was cast on a Teflon plate in dry inert gas atmosphere and the methyl ethyl ketone was evaporated off. The resultant layer was heated at 80°C to thereby polymerize and cure the methacrylic acid-2-hydroxyethyl methylcarbonate. Thus, a polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt (LiBF₄) was obtained.

Example 24

5.0 g of methacrylic acid-2-hydroxyethyl methylcarbonate produced in Example 1, 2.5 g of diethylene glycol dimethacrylate (produced by Shin-Nakamura Chemical Co., Ltd.), 0.5 g of LiN(CF₃SO₂)₂ and 5.0 g of methyl ethyl ketone were mixed together. The thus obtained homogeneous solution was cast on a glass plate in dry inert gas atmosphere and the methyl ethyl ketone was evaporated off. The resultant layer was irradiated with electron beams in dry inert gas atmosphere to thereby polymerize and cure the methacrylic acid-2-hydroxyethyl methylcarbonate together with the diethylene glycol dimethacrylate. Thus, a polymeric solid electrolyte composed of the acrylic ester copolymer and the Group Ia metal salt [LiN(CF₃SO₂)₂] was obtained.

Example 25

A polymeric solid electrolyte was produced in the same manner as in Example 24 except that propylene carbonate was employed in place of methyl ethyl ketone and that the propylene carbonate was not evaporated off.

Example 26Synthesis of di-2-methacryloxyethyl carbonate

13.01 g (0.1 mol) of hydroxyethyl methacrylate, 28.60 g (0.1 mol) of methacrylic acid-2-hydroxyethyl methylcarbonate and 0.042 g (0.3 mmol) of potassium carbonate as a catalyst were charged into a 100 ml four-necked flask and reacted at 90°C for 8 hr under reflux under agitation with removing formed methanol. After the completion of the reaction, potassium carbonate was removed by the use of a silica gel column and distillation was performed, thereby obtaining di-2-methacryloxyethyl carbonate.

Identification of the obtained di-2-methacryloxyethyl carbonate was conducted by NMR and IR. NMR and IR spectra are shown in Figs. 6 and 7, respectively.

NMR (CDCl₃ solution, δ ppm): 1.95 (t, 6H, J=0.8 Hz, CH₃), 4.40 (m, 8H, CH₂), 5.60 (t, 2H, J=1.1 Hz, CH), 6.14 (t, 2H, J=1.1 Hz, CH).

IR (neat, cm⁻¹): 2980 (C-H), 1760 (C=O), 1738 (C=O), 1640 (C=C), 1460, 1265, 1163, 1038, 950, 818, 795.

Example 27Preparation of acrylic ester polymer

2.86 g (0.01 mol) of di-2-methacryloxyethyl carbonate produced in Example 26 was mixed with 41.6 μ l of Peroyl IPP50 (produced by Nippon Oil & Fats Co., Ltd.). The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a transparent solid. A polymerization was confirmed by the extinction of absorption at 1640 cm⁻¹ ascribed to C=C vibration in an IR spectrum of the solid.

Example 28Preparation of di-2-methacryloxyethyl carbonate copolymer

1.43 g (0.005 mol) of di-2-methacryloxyethyl carbonate produced in Example 26, 0.94 g (0.005 mol) of methoxyethoxyethyl methacrylate and 41.6 μ l of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a transparent solid. A polymerization was confirmed by the extinction of absorption at 1640 cm⁻¹ ascribed to C=C vibration in an IR spectrum of the solid.

Example 29

A copolymer was prepared in the same manner as in Example 28 except that diethylene glycol dimethacrylate was employed in place of methoxyethoxyethyl methacrylate. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the copolymer, as in Example 28.

The obtained IR spectrum is shown in Fig. 8.

Example 30

A copolymer was prepared in the same manner as in Example 28 except that methacrylic acid-2-hydroxyethyl methylcarbonate was employed in place of methoxyethoxyethyl methacrylate.

Example 31

A copolymer was prepared in the same manner as in Example 28 except that methacrylic acid-2-hydroxyethoxyethyl methylcarbonate was employed in place of methoxyethoxyethyl methacrylate.

Example 32Production of polymeric electrolyte and measurement of ionic conductivity

50% by weight of di-2-methacryloxyethyl carbonate produced in Example 26, 50% by weight of propylene carbonate, 2 mol%, based on the carbonate units, of Group Ia metal salt of the formula $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 1 mol%, based on the monomers, of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the electrolyte.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 2.

Example 33

A polymeric solid electrolyte was produced in the same manner as in Example 32 except that di-2-methacryloxyethyl carbonate and propylene carbonate were used in respective amounts of 30% by weight and 70% by weight.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 2.

Example 34

70% by weight of a 1:9 (mol:mol) monomer mixture of di-2-methacryloxyethyl carbonate produced in Example 26 and methoxyethoxyethyl methacrylate, 30% by weight of propylene carbonate, 2 mol%, based on the carbonate units, of Group Ia metal salt of the formula $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 1 mol%, based on the monomers, of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the electrolyte.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 2.

Example 35

A polymeric solid electrolyte was produced in the same manner as in Example 34 except that methacrylic acid-2-hydroxyethyl methylcarbonate was employed in place of methoxyethoxyethyl methacrylate.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 2.

Example 36

A polymeric solid electrolyte was produced in the same manner as in Example 34 except that methacrylic acid-2-

hydroxyethoxyethyl methylcarbonate was employed in place of methoxyethoxyethyl methacrylate.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 2.

5 Example 37

50% by weight of a 5:5 (mol:mol) monomer mixture of di-2-methacryloxyethyl carbonate produced in Example 26 and diethylene glycol monomethacrylate, 50% by weight of propylene carbonate, 2 mol%, based on the carbonate units, of Group Ia metal salt of the formula $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 1 mol%, based on the monomers, of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 70°C in inert gas atmosphere for 24 hr, thereby obtaining a polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the electrolyte.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 2.

Example 38

A polymeric solid electrolyte was produced in the same manner as in Example 37 except that the monomer mixture and propylene carbonate were used in respective amounts of 30% by weight and 70% by weight.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 2.

Table 2

Measurement of Ionic Conductivity	
Example	Conductivity (S/cm)
32	7.2×10^{-7}
33	2.5×10^{-3}
34	2.1×10^{-5}
35	3.1×10^{-6}
36	8.8×10^{-6}
37	1.1×10^{-5}
38	2.0×10^{-3}

Example 39

45 Production of polymeric solid electrolyte

5.0 g of di-2-methacryloxyethyl carbonate produced in Example 26, 0.5 g of LiClO_4 , 5.0 g of methyl ethyl ketone and 0.005 g of benzophenone were mixed together. The thus obtained homogeneous solution was cast on a glass plate in dry inert gas atmosphere and the methyl ethyl ketone was evaporated off. The resultant layer was irradiated with ultraviolet rays in dry inert gas atmosphere to thereby polymerize and cure the di-2-methacryloxyethyl carbonate. Thus, a polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt (LiClO_4) was obtained.

Example 40

A polymeric solid electrolyte was produced in the same manner as in Example 39 except that propylene carbonate was employed in place of methyl ethyl ketone and that the propylene carbonate was not evaporated off.

Example 41

5.0 g of di-2-methacryloxyethyl carbonate produced in Example 26, 0.5 g of $\text{LiOSO}_2\text{CF}_3$, 5.0 g of methyl ethyl ketone and 0.025 g of benzoyl peroxide were mixed together. The thus obtained homogeneous solution was cast on a Teflon plate in dry inert gas atmosphere and the methyl ethyl ketone was evaporated off. The resultant layer was heated at 80°C to thereby polymerize and cure the di-2-methacryloxyethyl carbonate. Thus, a polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt ($\text{LiOSO}_2\text{CF}_3$) was obtained.

Example 42

5.0 g of di-2-methacryloxyethyl carbonate produced in Example 26, 2.5 g of diethylene glycol dimethacrylate (produced by Shin-Nakamura Chemical Co., Ltd.), 0.5 g of LiBF_4 and 5.0 g of methyl ethyl ketone were mixed together. The thus obtained homogeneous solution was cast on a glass plate in dry inert gas atmosphere and the methyl ethyl ketone was evaporated off. The resultant layer was irradiated with electron beams in dry inert gas atmosphere to thereby polymerize and cure the di-2-methacryloxyethyl carbonate together with the diethylene glycol dimethacrylate. Thus, a polymeric solid electrolyte composed of the acrylic ester copolymer and the Group Ia metal salt (LiBF_4) was obtained.

Example 43

A polymeric solid electrolyte was produced in the same manner as in Example 42 except that propylene carbonate was employed in place of methyl ethyl ketone and that the propylene carbonate was not evaporated off.

Example 44Synthesis of 2-methoxyethoxyethoxyethyl allyl carbonate

14.2 g (0.1 mol) of diallyl carbonate, 49.2 g (0.3 mol) of triethylene glycol monomethyl ester and 0.042 g (0.3 mmol) of potassium carbonate as a catalyst were charged into a 100 ml four-necked flask and reacted at 130°C for 8 hr under reflux under agitation with removing formed allyl alcohol. After the completion of the reaction, potassium carbonate was removed by the use of a silica gel column and distillation was performed, thereby obtaining 2-methoxyethoxyethoxyethyl allyl carbonate.

Identification of the obtained 2-methoxyethoxyethoxyethyl allyl carbonate was conducted by NMR and IR. NMR and IR spectra are shown in Figs. 9 and 10, respectively.

NMR (CDCl_3 solution, δ ppm): 3.39 (s, 3H, CH_3), 3.55 - 3.78 (m, 10H, CH_2), 4.30 (t, 2H, $J=1.3$ Hz, CH_2), 4.64 (d, 2H, $J=3.2$ Hz, CH_2), 5.28 (d, 1H, $J=4.0$ Hz, CH), 5.38 (d, 1H, $J=6.0$ Hz, CH), 5.93 (m, 1H, CH).
IR (neat, cm^{-1}): 2880 (C-H), 1748 (C=O), 1649 (C=C), 1451, 1383, 1260, 1108, 872, 787.

Example 45Synthesis of methoxyethyl allyloxyethyl carbonate

23.0 g (0.1 mol) of di-2-allyloxyethyl carbonate, 22.8 g (0.3 mol) of methoxyethanol and 0.042 g (0.3 mmol) of potassium carbonate as a catalyst were charged into a flask and reacted at 130°C for 8 hr under reflux under agitation with removing formed allyloxyethanol. After the completion of the reaction, potassium carbonate was removed by the use of a silica gel column and distillation was performed, thereby obtaining methoxyethyl allyloxyethyl carbonate.

Identification of the obtained methoxyethyl allyloxyethyl carbonate was conducted by NMR and IR. NMR and IR spectra are shown in Figs. 11 and 12, respectively.

NMR (CDCl_3 solution, δ ppm): 3.22 (s, 3H, CH_3), 3.60 - 3.68 (m, 4H, CH_2), 4.01 (m, 2H, CH_2), 4.26 - 4.31 (m, 4H, CH_2), 5.20 (d, 1H, $J=4$ Hz, CH), 5.30 (d, 1H, $J=6$ Hz, CH), 5.89 (m, 1H, CH).
IR (neat, cm^{-1}): 2890 (C-H), 1749 (C=O), 1646 (C=C), 1451, 1263, 1127, 1029, 786.

Example 46Preparation of allyl carbonate polymer

2.48 g (0.01 mol) of 2-methylethoxyethoxyethyl allyl carbonate synthesized in Example 44, 41.6 μl Peroyl IPP50 (produced by Nippon Oil & Fats Co., Ltd.) were mixed together. The thus obtained homogeneous liquid was cast on a

Teflon-coated glass plate and cured at 70 °C in inert gas atmosphere for 24 hr, thereby obtaining a transparent solid. A polymerization was confirmed by the extinction of absorption at 1640 cm⁻¹ ascribed to C=C vibration in an IR spectrum of the solid.

5 Example 47

Preparation of allyl carbonate copolymer

1.24 g (0.005 mol) of 2-methoxyethoxyethoxyethyl allyl carbonate synthesized in Example 44, 0.58 g (0.005 mol) of methyl allyl carbonate and 41.6 µl of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 80°C in inert gas atmosphere for 24 hr, thereby obtaining a transparent solid. A polymerization was confirmed by the extinction of absorption at 1640 cm⁻¹ ascribed to C=C vibration in an IR spectrum of the solid.

15 Example 48

A copolymer was prepared in the same manner as in Example 47 except that diallyl carbonate was employed in place of methyl allyl carbonate. A polymerization was confirmed by the extinction of absorption at 1640 cm⁻¹ ascribed to C=C vibration in an IR spectrum of the copolymer, as in Example 47.

20 The obtained IR spectrum is shown in Fig. 13.

Example 49

Production of polymeric electrolyte and measurement of ionic conductivity

50% by weight of a 5:5 (mol:mol) monomer mixture of 2-methoxyethoxyethoxyethyl allyl carbonate synthesized in Example 44 and diallyl carbonate, 1 mol%, based on the carbonate units, of Group Ia metal salt of the formula LiN(CF₃SO₂)₂ and 1 mol%, based on the monomers, of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 80°C in inert gas atmosphere for 24 hr, thereby obtaining a polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt. A polymerization was confirmed by the extinction of absorption at 1640 cm⁻¹ ascribed to C=C vibration in an IR spectrum of the electrolyte.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 3.

Table 3

Measurement of Ionic Conductivity	
Example	Conductivity (S/cm)
49	9.5×10^{-4}

45 Example 50

Production of polymeric electrolyte

5.0 g of 2-methoxyethyl allyl carbonate produced in Example 44, 0.5 g of LiBF₄, 5.0 g of dimethyl carbonate and 0.2 g of diisopropyl peroxydicarbonate as a polymerization catalyst were mixed together. The thus obtained homogeneous solution was cast on a glass plate in dry inert gas atmosphere and the dimethyl carbonate was evaporated off. The resultant layer was heated at 80°C, thereby obtaining a polymeric electrolyte composed of the 2-methoxyethyl allyl carbonate polymer and the Group Ia metal salt.

55 Example 51

A polymeric electrolyte was produced in the same manner as in Example 50 except that propylene carbonate was employed in place of dimethyl carbonate and that the propylene carbonate was not evaporated off.

Example 52

A polymeric electrolyte was produced in the same manner as in Example 50 except that LiClO_4 was employed in place of LiBF_4 .

Example 53Synthesis of diethylene glycol diallyl dicarbonate

28.4 g (0.2 mol) of diallyl carbonate, 10.6 g (0.1 mol) of diethylene glycol and 0.042 g (0.3 mmol) of potassium carbonate as a catalyst were charged into a 100 ml four-necked flask and reacted at 130°C for 8 hr under reflux under agitation with removing formed allyl alcohol. After the completion of the reaction, potassium carbonate was removed by the use of a silica gel column and distillation was performed, thereby obtaining diethylene glycol diallyl dicarbonate.

Identification of the obtained diethylene glycol diallyl dicarbonate was conducted by NMR and IR. NMR and IR spectra are shown in Figs. 14 and 15, respectively.

NMR (CDCl_3 solution, δ ppm): 3.73 (m, 4H, CH_2), 4.30 (m, 4H, CH_2), 4.62 (m, 4H, CH_2), 5.26 (q, 2H, $J=8.1$ Hz, CH), 5.33 (q, 2H, $J=13.5$ Hz, CH), 5.94 (m, 2H, CH_2).
IR (neat, cm^{-1}): 2958 (C-H), 1750 (C=O), 1649 (C=C), 1451, 1387, 1280, 1143, 876, 786.

Example 54Preparation of allyl carbonate polymer

2.88 g (0.01 mol) of diethylene glycol diallyl dicarbonate produced in Example 53 and 41.6 μl of Peroyl IPP50 (produced by Nippon Oil & Fats Co., Ltd.) were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 80°C in inert gas atmosphere for 24 hr, thereby obtaining a transparent solid. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the solid.

Example 55Preparation of allyl carbonate copolymer

1.44 g (0.005 mol) of diethylene glycol diallyl dicarbonate produced in Example 53, 1.24 g (0.005 mol) of 2-methoxyethoxyethoxyethyl allyl carbonate and 41.6 μl of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 80°C in inert gas atmosphere for 24 hr, thereby obtaining a transparent solid. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the solid.

Example 56

A copolymer was prepared in the same manner as in Example 55 except that methyl allyl carbonate was employed in place of 2-methoxyethoxyethoxyethyl allyl carbonate.

Example 57

A copolymer was prepared in the same manner as in Example 55 except that diallyl carbonate was employed in place of 2-methoxyethoxyethoxyethyl allyl carbonate. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the copolymer, as in Example 55.

The obtained IR spectrum is shown in Fig. 16.

Example 58Production of polymeric electrolyte and measurement of ionic conductivity

Diethylene glycol diallyl dicarbonate produced in Example 1, 2 mol%, based on the carbonate units, of Group Ia metal salt of the formula $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 1 mol%, based on the monomer, of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 80°C in inert gas atmosphere

for 24 hr, thereby obtaining a polymeric solid electrolyte composed of the allyl carbonate polymer and the Group Ia metal salt. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the electrolyte.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 4.

Example 59

A polymeric solid electrolyte was produced in the same manner as in Example 58 except that a mixture of 70% by weight of diethylene glycol diallyl dicarbonate and 30% by weight of propylene carbonate was employed.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 4.

Example 60

A 5:5 (mol:mol) monomer mixture of diethylene glycol diallyl dicarbonate produced in Example 53 and 2-methoxyethoxyethoxyethyl allyl carbonate, 2 mol%, based on the carbonate units, of Group Ia metal salt of the formula $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and 1 mol%, based on the monomers, of Peroyl IPP50 were mixed together. The thus obtained homogeneous liquid was cast on a Teflon-coated glass plate and cured at 80°C in inert gas atmosphere for 24 hr, thereby obtaining a thin-film polymeric solid electrolyte composed of the acrylic ester polymer and the Group Ia metal salt. A polymerization was confirmed by the extinction of absorption at 1640 cm^{-1} ascribed to C=C vibration in an IR spectrum of the electrolyte.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 4.

Example 61

A polymeric solid electrolyte was produced in the same manner as in Example 60 except that methyl allyl carbonate was employed in place of 2-methoxyethoxyethoxyethyl allyl carbonate.

The ionic conductivity of the obtained thin-film polymeric solid electrolyte was measured in the same manner as in Example 12. The results are given in Table 4.

Example 62

A polymeric solid electrolyte was produced in the same manner as in Example 60 except that diallyl carbonate was employed in place of 2-methoxyethoxyethoxy-ethyl allyl carbonate.

Table 4

Measurement of Ionic Conductivity	
Example	Conductivity (S/cm)
58	1.9×10^{-6}
59	1.5×10^{-4}
60	2.2×10^{-4}
61	2.7×10^{-6}
62	2.1×10^{-6}

Example 63

Synthesis of diethylene glycol diallyl dicarbonate

Diethylene glycol diallyl dicarbonate was synthesized in the same manner as in Example 53 except that the amount of diallyl carbonate was varied to 14.2 g (0.1 mol).

Example 64Production of polymeric electrolyte

5 5.0 g of diethylene glycol diallyl dicarbonate produced in Example 53, 0.5 g of LiBF_4 , 5.0 g of dimethyl carbonate and 0.2 g of diisopropyl peroxydicarbonate as a polymerization catalyst were mixed together. The thus obtained homogeneous solution was cast on a glass plate in dry inert gas atmosphere and the dimethyl carbonate was evaporated off. The resultant layer was heated at 80°C to thereby polymerize the diethylene glycol diallyl dicarbonate and cure the resulting polymer. Thus, a polymeric electrolyte composed of the diethylene glycol diallyl dicarbonate polymer and the

10 Group Ia metal salt was obtained.

Example 65

A polymeric electrolyte was produced in the same manner as in Example 64 except that propylene carbonate was employed in place of dimethyl carbonate and that the propylene carbonate was not evaporated off.

15

Example 66

A polymeric electrolyte was produced in the same manner as in Example 64 except that LiClO_4 was employed in place of LiBF_4 .

20

Example 67Synthesis of allyl methyl carbonate

25 422 g (7.27 mol) of allyl alcohol, 2120 g (23.6 mol) of dimethyl carbonate and 1.0 g (7.3 mmol) of potassium carbonate as a catalyst were charged into a 5 lit. four-necked flask and reacted at 90°C for 10 hr under reflux under agitation with removing formed methanol. After the completion of the reaction, potassium carbonate was removed by the use of a short column of silica gel, and then distillation was performed, thereby obtaining allyl methyl carbonate.

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Synthesis of trifunctional compound

23 g of glycerol, 2.5 g of potassium hydroxide and 1200 g of ethylene oxide were charged into an autoclave and reacted at 130°C for 7 hr. Neutralization and desalting were conducted, thereby obtaining a trifunctional polyethylene oxide of about 6000 in molecular weight having a hydroxyl group at its terminal. 2 g of concentrated sulfuric acid and toluene were added to 200 g of this trifunctional polyethylene oxide and 15 g of methacrylic acid and a dehydrating condensation was carried out with azeotropically distilling water off under reflux. Thus, trifunctional compound of the above general formula (VII) wherein R^{22} , R^{23} and R^{24} represent hydrogen atoms and R^{25} , R^{26} and R^{27} represent methyl groups was obtained.

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Production of polymeric solid electrolyte

5.0 g of allyl methyl carbonate and 2.0 g of trifunctional compound synthesized above, 5.0 g of LiBF_4 , 5.0 g of dimethyl carbonate and 0.2 g of diisopropyl peroxydicarbonate were mixed together. The thus obtained homogeneous solution was cast on a glass plate in dry inert gas atmosphere and the dimethyl carbonate was evaporated off. The resultant layer was heated at 80°C to thereby copolymerize the allyl methyl carbonate and trifunctional compound and cure the resulting polymer. Thus, a polymeric solid electrolyte composed of the allyl carbonate copolymer and the Group Ia metal salt (LiBF_4) was obtained.

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Example 68

A polymeric solid electrolyte was produced in the same manner as in Example 67 except that propylene carbonate was employed in place of dimethyl carbonate and that the propylene carbonate was not evaporated off.

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Example 69

A polymeric solid electrolyte was produced in the same manner as in Example 70 except that propylene carbonate was employed in place of dimethyl carbonate, that LiClO_4 was employed in place of LiBF_4 and that the propylene carbonate was not evaporated off.

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Example 70Synthesis of diallyl carbonate

842 g (14.5 mol) of allyl alcohol, 1306 g (14.5 mol) of dimethyl carbonate and 1.0 g (7.3 mmol) of potassium carbonate as a catalyst were charged into a 3 lit. four-necked flask and reacted at 90°C for 10 hr under reflux under agitation with removing formed methanol. After the completion of the reaction, potassium carbonate was removed by the use of a short column of silica gel, and then distillation was performed, thereby obtaining diallyl carbonate.

10 Production of polymeric solid electrolyte

5.0 g of diallyl carbonate synthesized above, 2.0 g of trifunctional compound synthesized in Example 67, 5.0 g of LiBF₄, 5.0 g of dimethyl carbonate and 0.2 g of diisopropyl peroxydicarbonate were mixed together. The thus obtained homogeneous solution was cast on a glass plate in dry inert gas atmosphere and the dimethyl carbonate was evaporated off. The resultant layer was heated at 80°C to thereby copolymerize the diallyl carbonate and trifunctional compound and cure the resulting polymer. Thus, a polymeric solid electrolyte composed of the allyl carbonate copolymer and the Group Ia metal salt (LiBF₄) was obtained.

Example 71

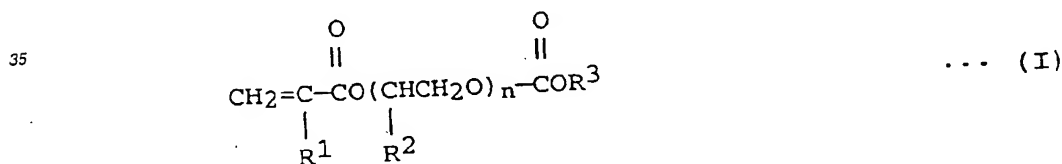
20 A polymeric solid electrolyte was produced in the same manner as in Example 70 except that propylene carbonate was employed in place of dimethyl carbonate and that the propylene carbonate was not evaporated off.

Example 72

25 A polymeric solid electrolyte was produced in the same manner as in Example 70 except that propylene carbonate was employed in place of dimethyl carbonate, that LiClO₄ was employed in place of LiBF₄ and that the propylene carbonate was not evaporated off.

30 **Claims**

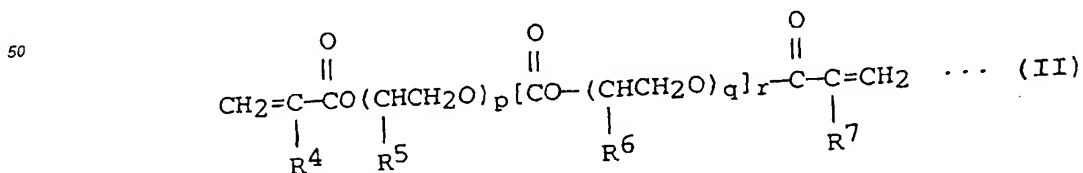
1. An acrylic ester represented by the general formula:



wherein

R¹ and R² may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; R³ represents an alkyl group having 1 to 4 carbon atoms; and n is an integer of 1 to 100.

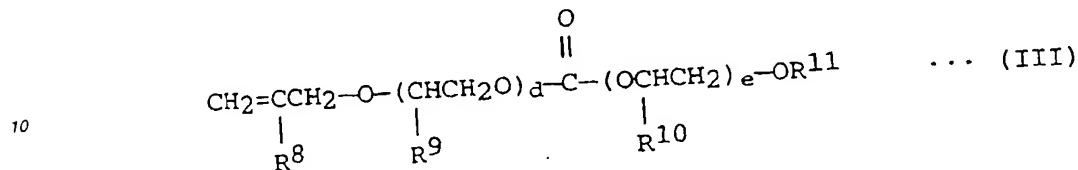
2. An acrylic ester represented by the general formula:



wherein

R^4 to R^7 may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and p, q and r may be identical with or different from each other and each is an integer of 1 to 100.

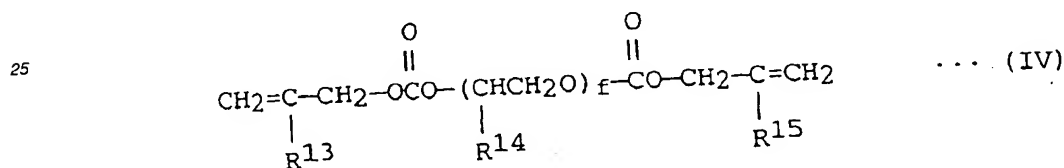
- 5 3. An allyl ether represented by the general formula:



15 wherein

R^8 , R^9 and R^{10} may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; R^{11} represents an alkyl group having 1 to 4 carbon atoms or $\text{CH}_2\text{CR}^{12}=\text{CH}_2$ in which R^{12} represents hydrogen atom or a methyl group; d is an integer of 0 to 100; and e is an integer of 1 to 100.

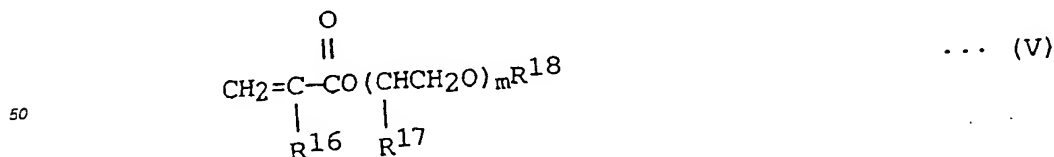
- 20 4. An allyl carbonate represented by the general formula:



30 wherein

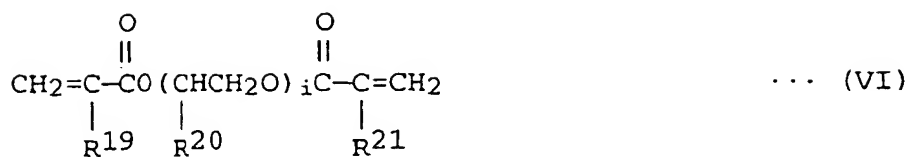
R^{13} , R^{14} and R^{15} may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and f is an integer of 0 to 100.

- 35 5. An acrylic ester polymer comprising structural units derived from at least one acrylic ester selected from a group of the acrylic esters of claim 1.
- 40 6. An acrylic ester polymer as claimed in claim 5, which is a homopolymer or copolymer of an acrylic ester selected from a group of the acrylic esters of claim 1.
- 45 7. An acrylic ester polymer as claimed in claim 5, which is a copolymer of at least one acrylic ester selected from a group of the acrylic esters of claim 1 and at least one compound selected from a group of the compounds represented by the above general formula (II) and the following general formula:



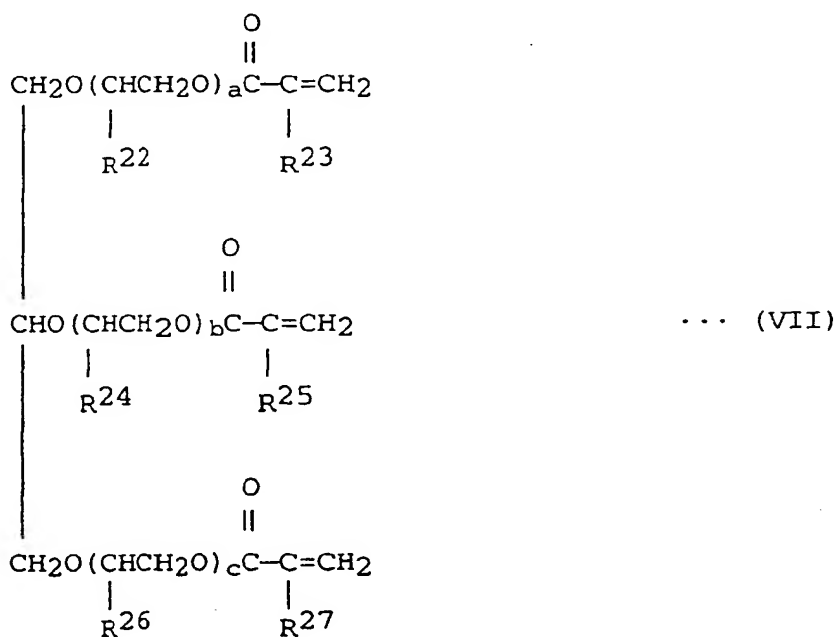
55 wherein

R^{16} and R^{17} may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; R^{18} represents an alkyl group having 1 to 100 carbon atoms; and m is an integer of 1 to 100.



wherein

R^{19} , R^{20} and R^{21} may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and i is an integer of 1 to 100,



wherein

R^{22} to R^{27} may be identical with or different from each other and each represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and a , b and c may be identical with or different from each other and each is an integer of 0 to 100, and



wherein

k is an integer of 1 to 100.

8. An acrylic ester polymer comprising structural units derived from at least one acrylic ester selected from a group of the acrylic esters of claim 2.
9. An acrylic ester polymer as claimed in claim 8, which is a homopolymer or copolymer of an acrylic ester selected from a group of the acrylic esters of claim 2.

10. An acrylic ester polymer as claimed in claim 8, which is a copolymer of at least one acrylic ester selected from a group of the acrylic esters of claim 2 and at least one compound selected from a group of the compounds represented by the above general formulae (V) to (VIII).

11. An allyl ether polymer comprising structural units derived from at least one allyl ether selected from a group of the allyl ethers of claim 3.

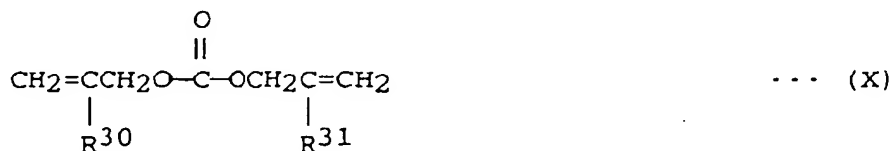
12. An allyl ether polymer as claimed in claim 11, which is a homopolymer or copolymer of an allyl ether selected from a group of the allyl ethers of claim 3.

13. A copolymer of at least one allyl ether selected from a group of the allyl ethers of claim 3 and at least one compound selected from a group of the compounds represented by the above general formulae (IV) and (VII) and the following general formula:



wherein

R^{28} represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms; and R^{29} represents an alkyl group having 1 to 4 carbon atoms, and



wherein

each of R^{30} and R^{31} represents hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

14. An allyl carbonate polymer comprising structural units derived from at least one allyl carbonate selected from a group of the allyl carbonates of claim 4.

15. An allyl carbonate polymer as claimed in claim 14, which is a homopolymer or copolymer of an allyl carbonate selected from a group of the allyl carbonates of claim 4.

16. An allyl carbonate polymer as claimed in claim 14, which is a copolymer of at least one allyl carbonate selected from a group of the allyl carbonates of claim 4 and at least one compound selected from a group of the compounds represented by the above general formula (VII).

17. An allyl carbonate copolymer comprising:

structural units derived from at least one compound selected from a group of the compounds represented by the above general formula (VII) and structural units derived from at least one compound selected from a group of the compounds represented by the above general formula (IX).

18. An allyl carbonate copolymer comprising:

structural units derived from at least one compound selected from a group of the compounds represented by the above general formula (VII) and structural units derived from at least one compound selected from a group of the compounds represented by the above general formula (X).

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19. A polymeric solid electrolyte comprising at least one member of the acrylic ester polymers, allyl ether polymers and allyl carbonate polymers of claims 5 to 18 and a salt of a metal of Group Ia of the periodic table.

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20. A gelled polymeric solid electrolyte comprising at least one member of the acrylic ester polymers, allyl ether polymers and allyl carbonate polymers of claims 5 to 18, a salt of a metal of Group Ia of the periodic table and a non-aqueous solvent.

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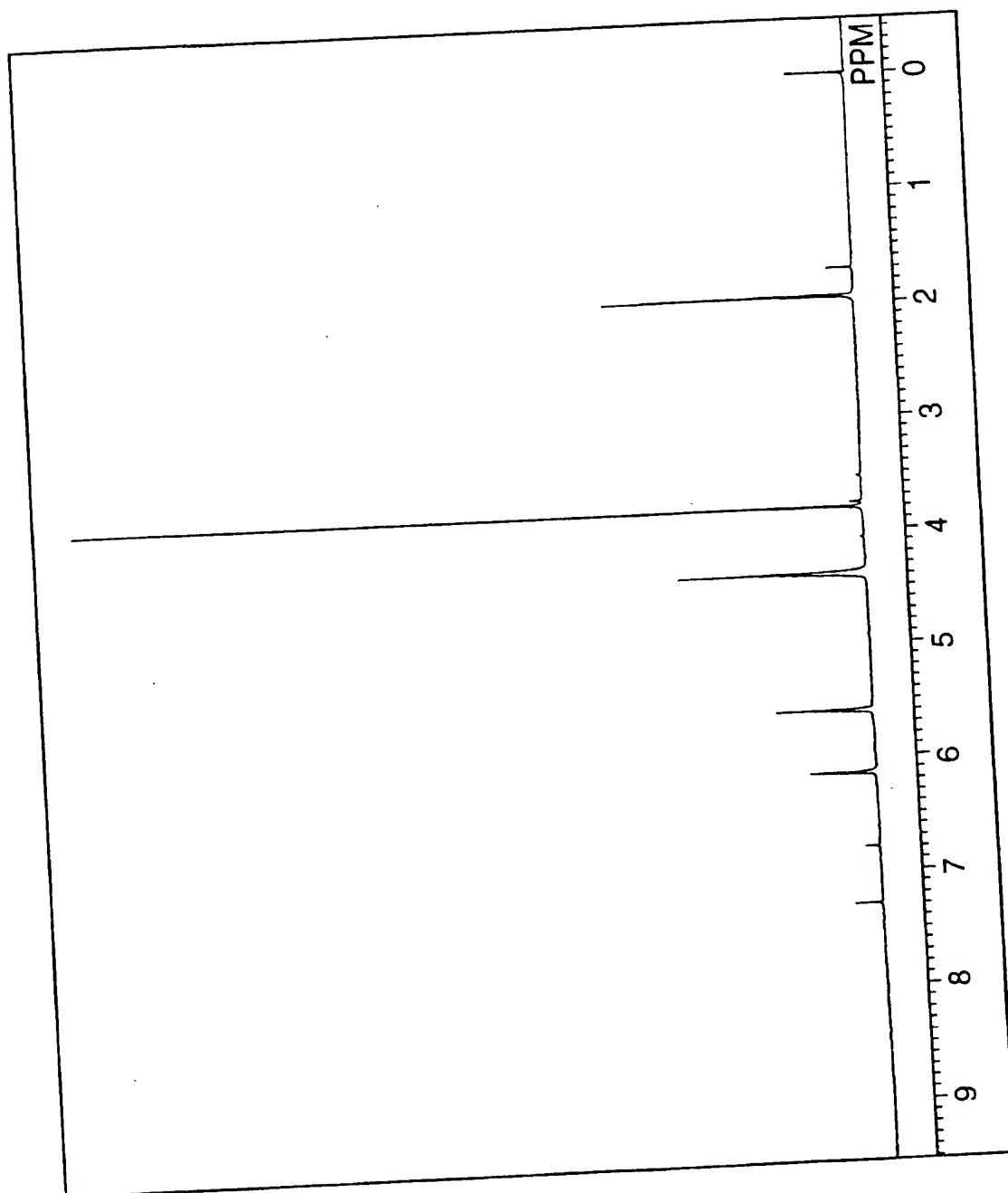
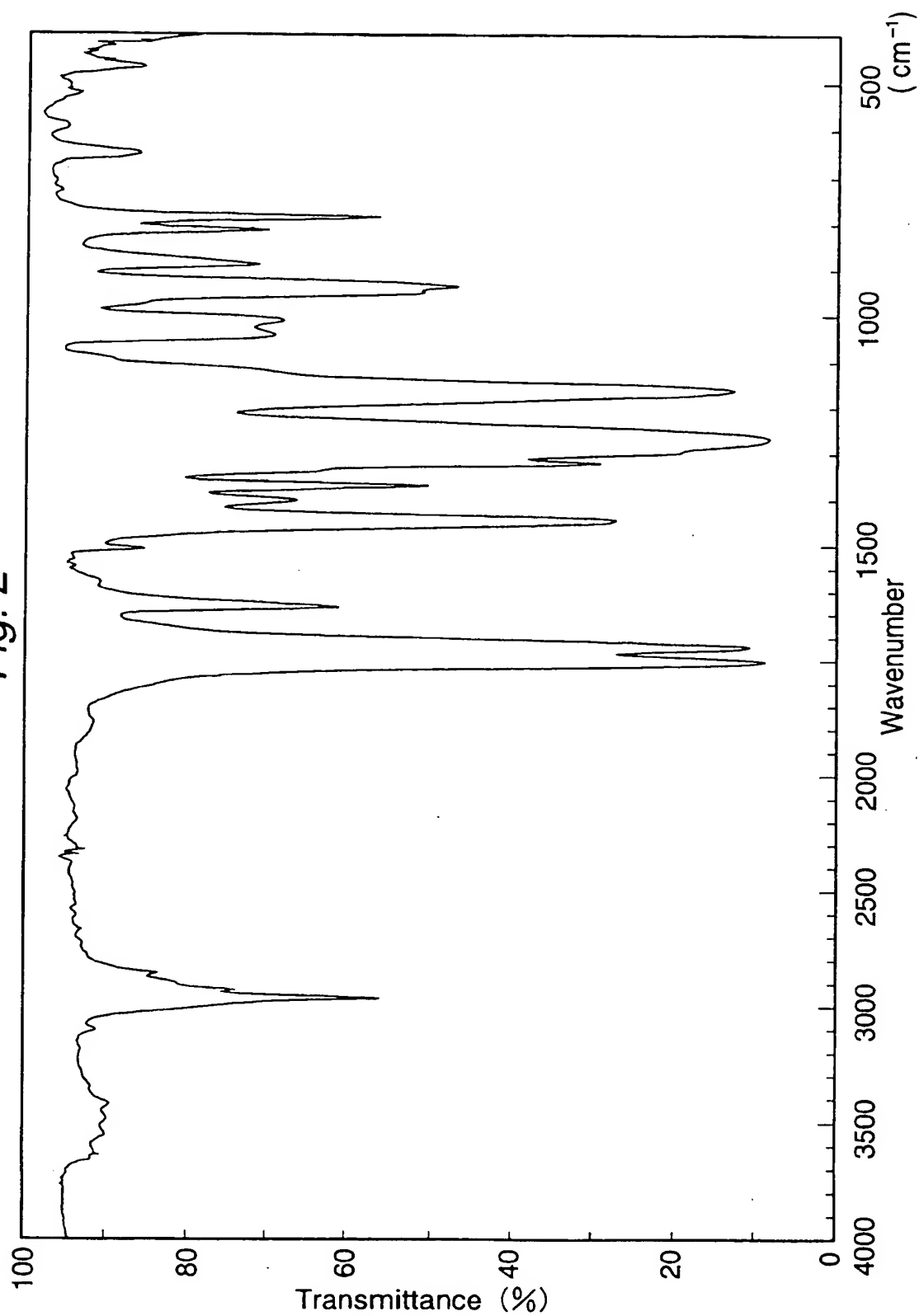


Fig. 1

Fig. 2



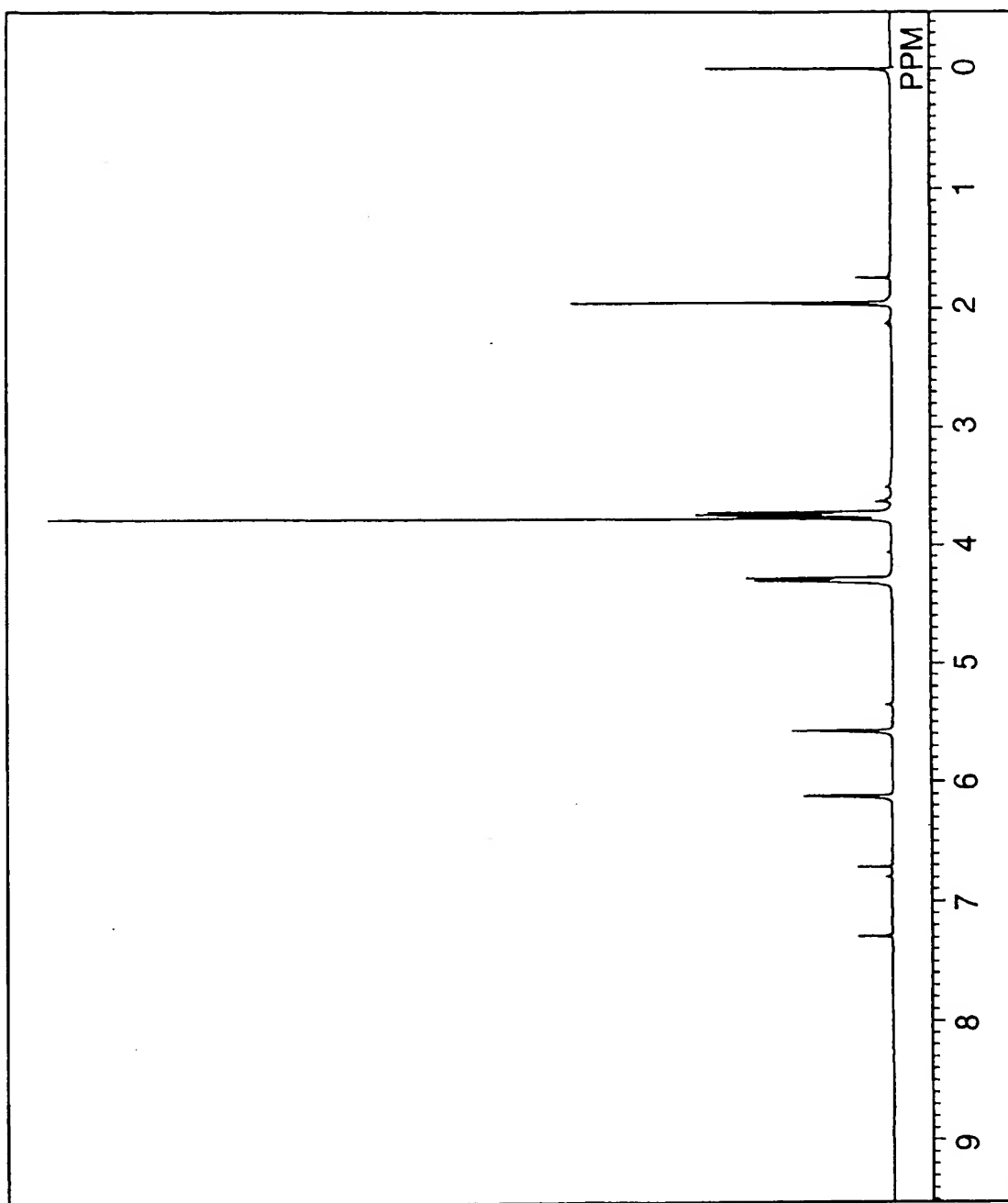


Fig. 3

Fig. 4

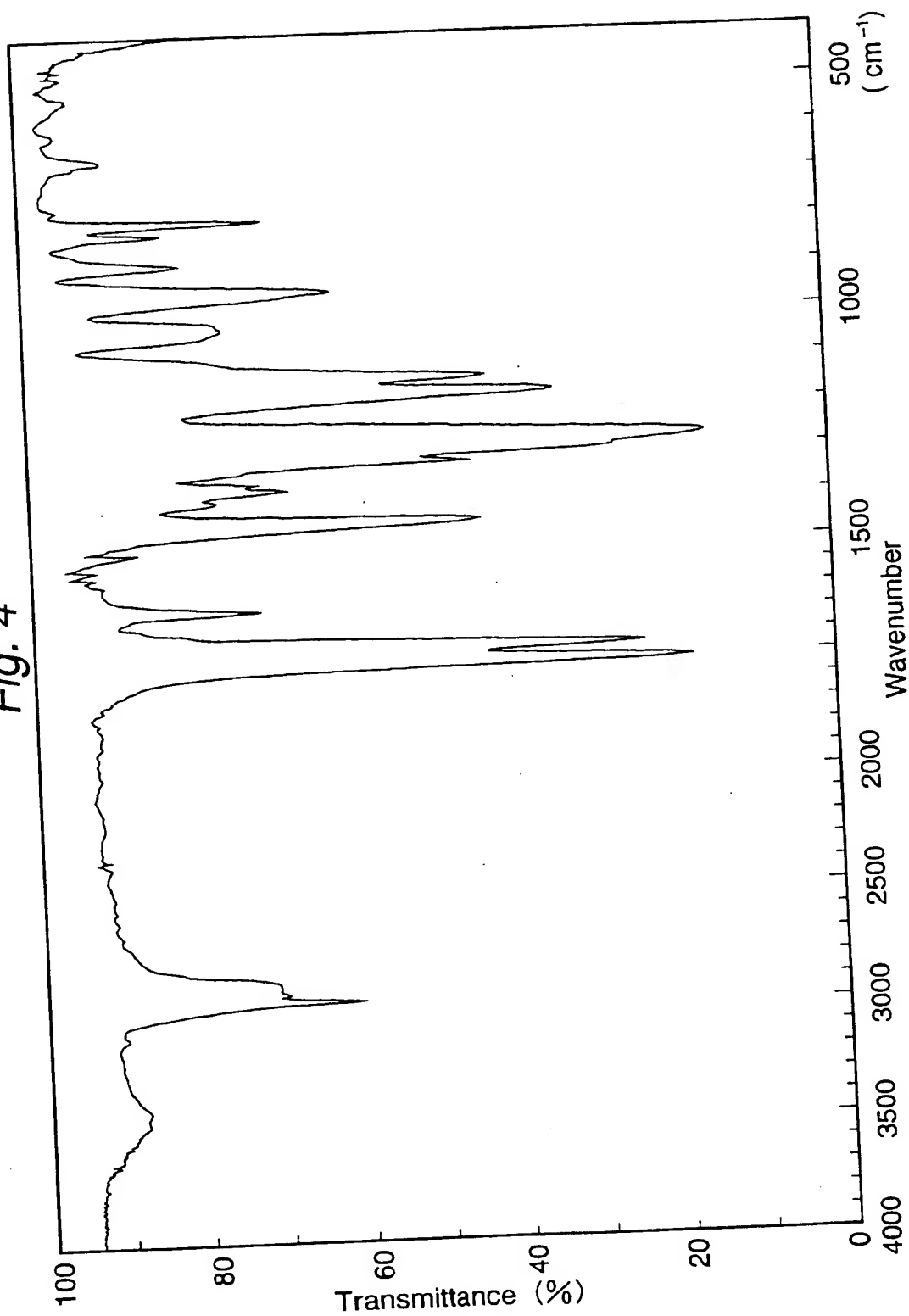
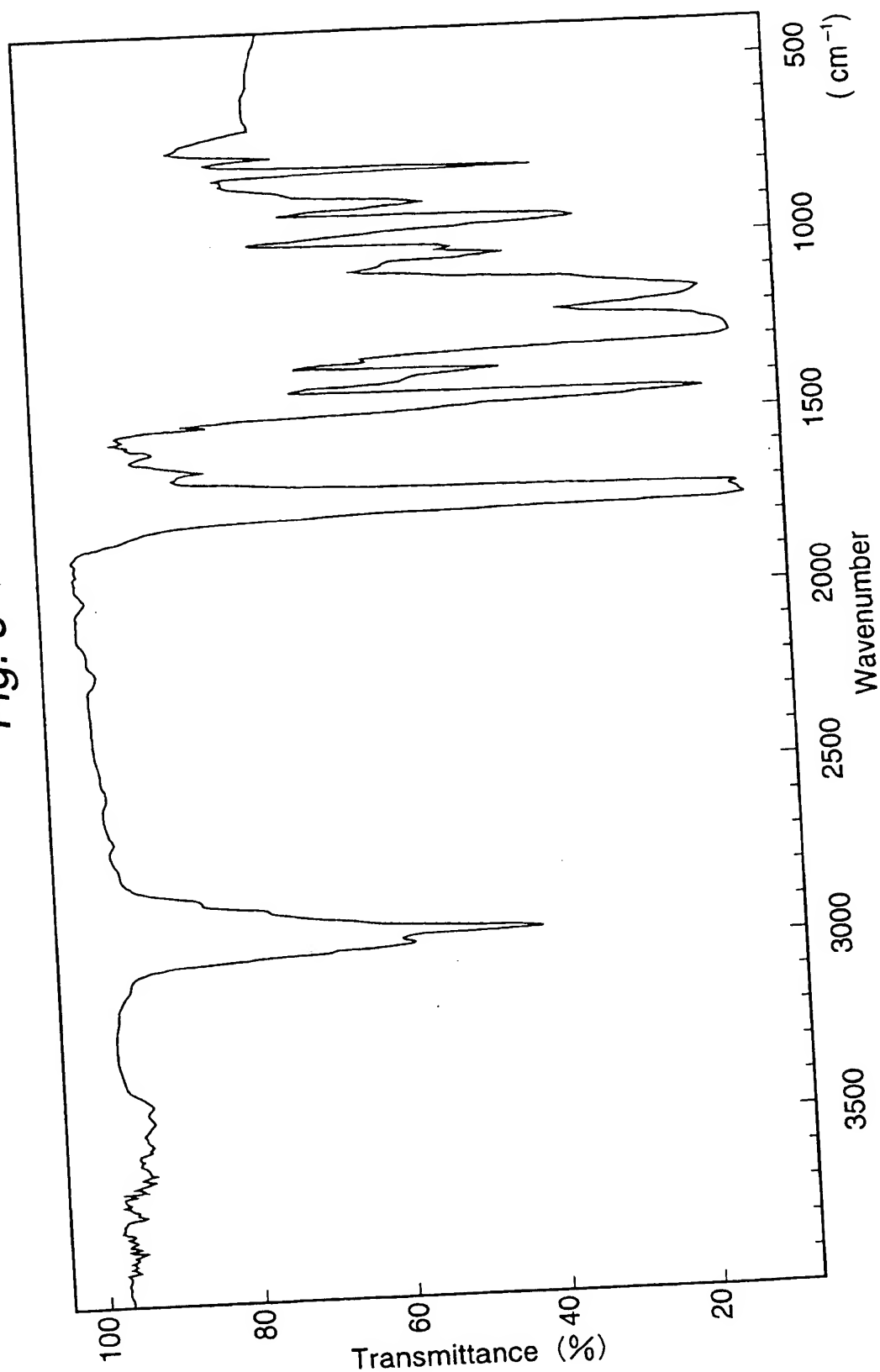


Fig. 5



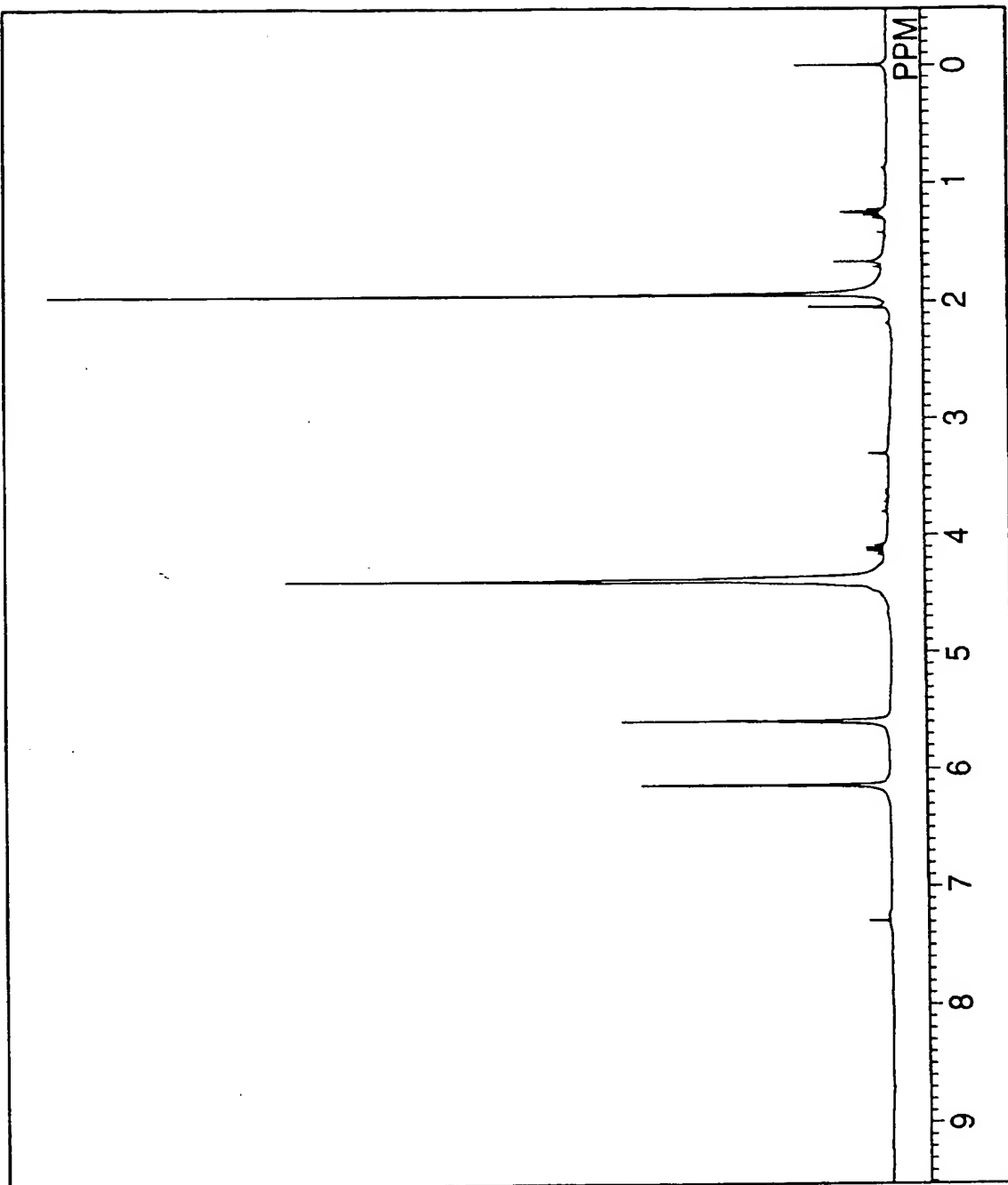


Fig. 6

Fig. 7

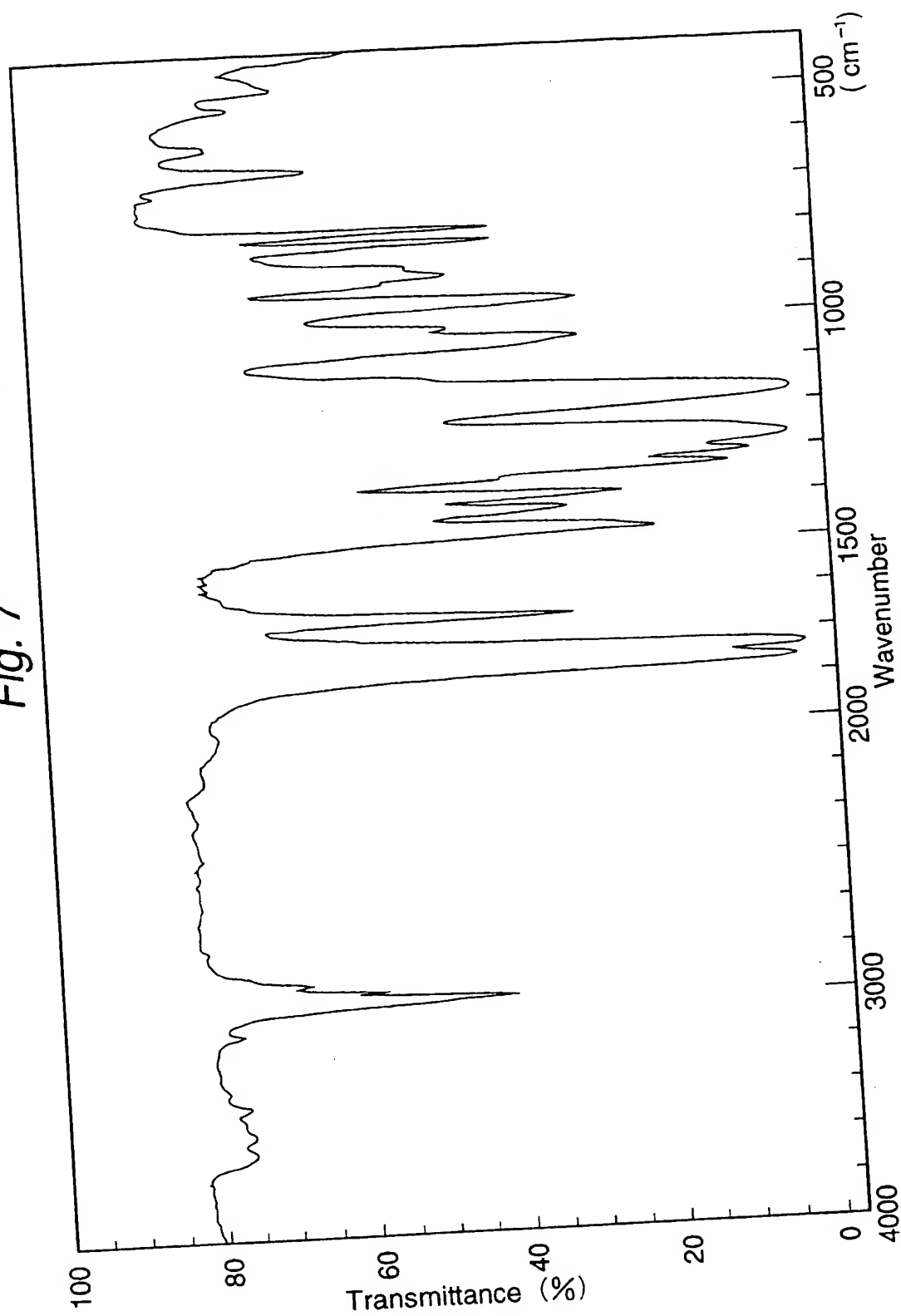
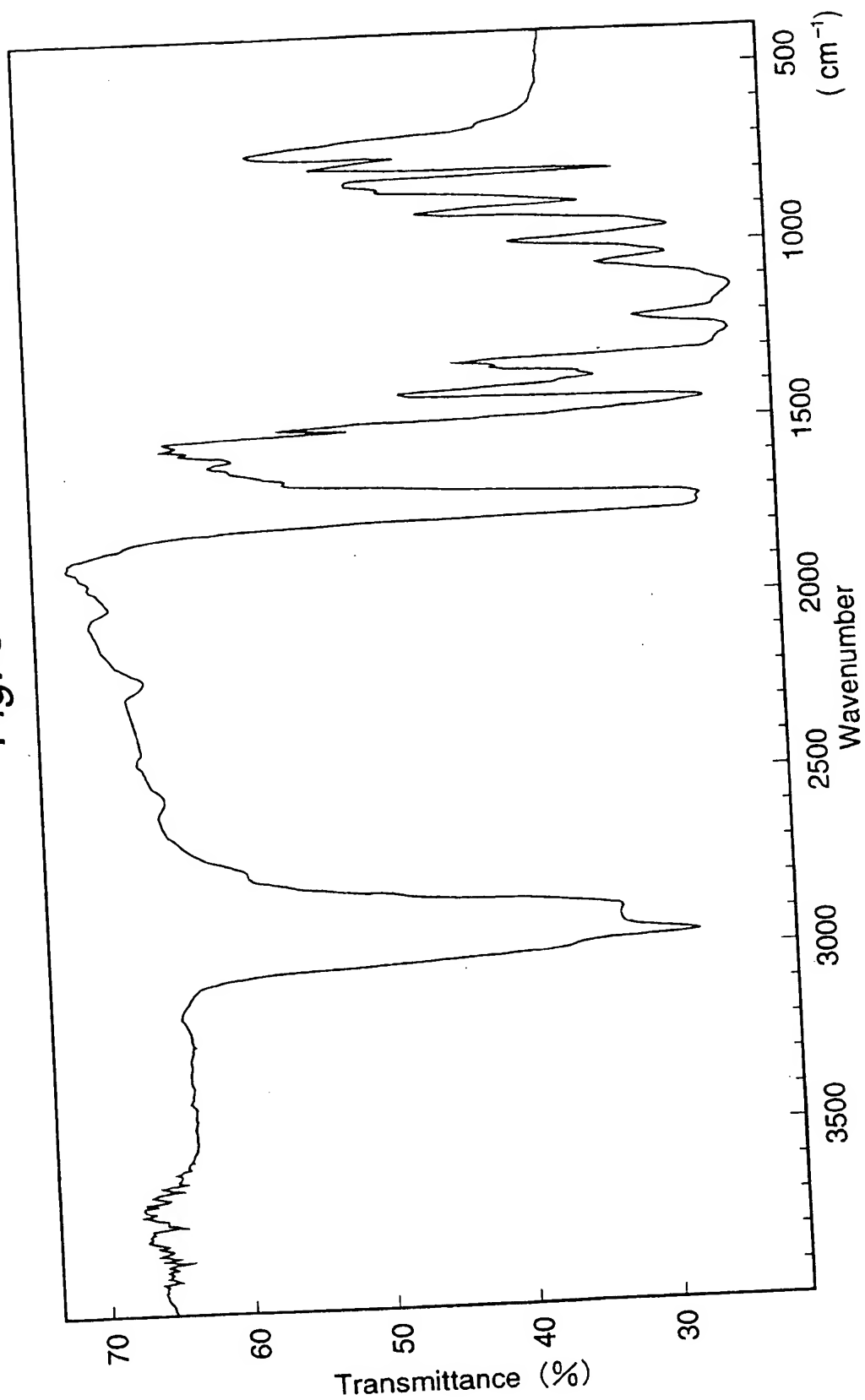


Fig. 8



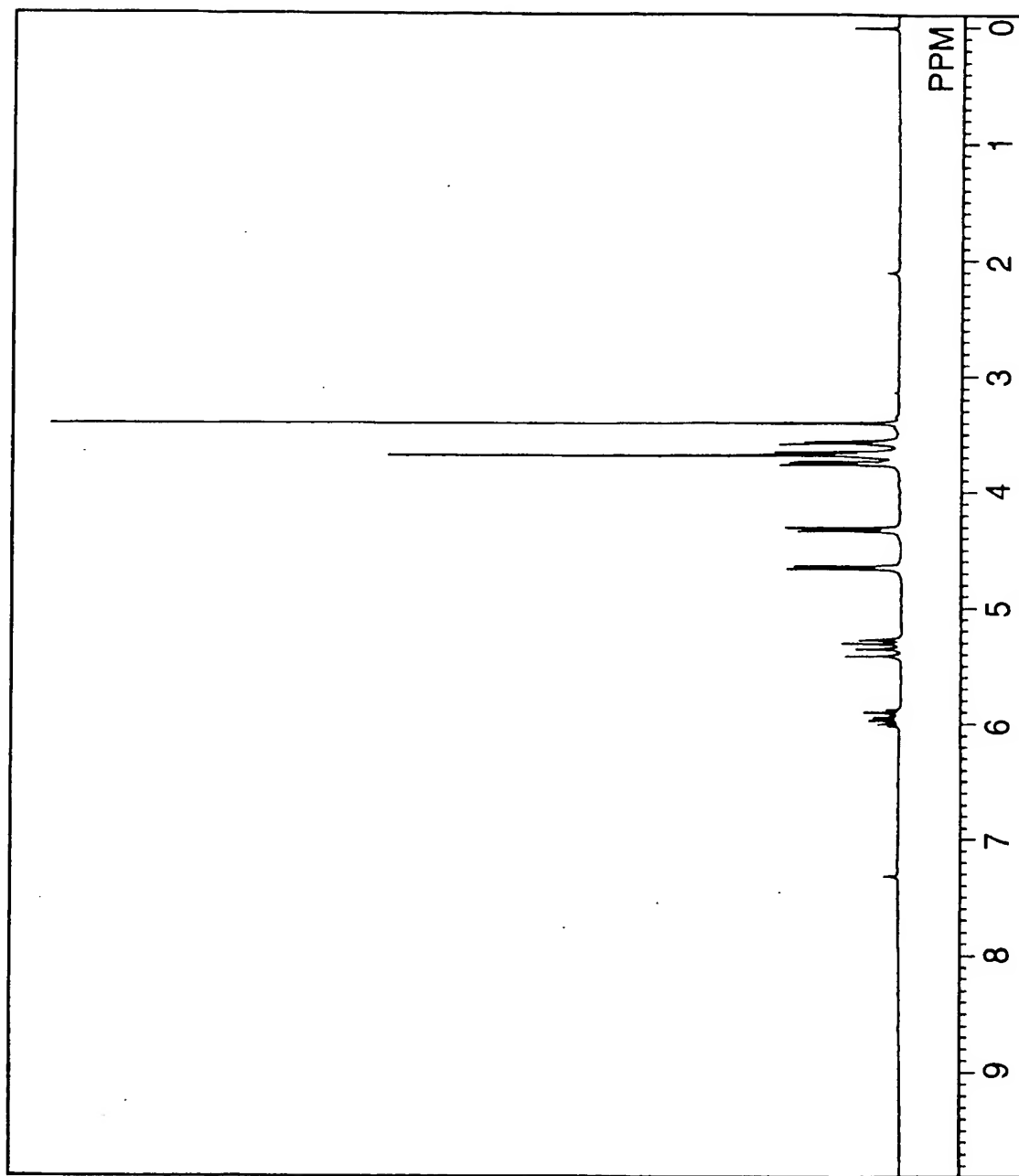
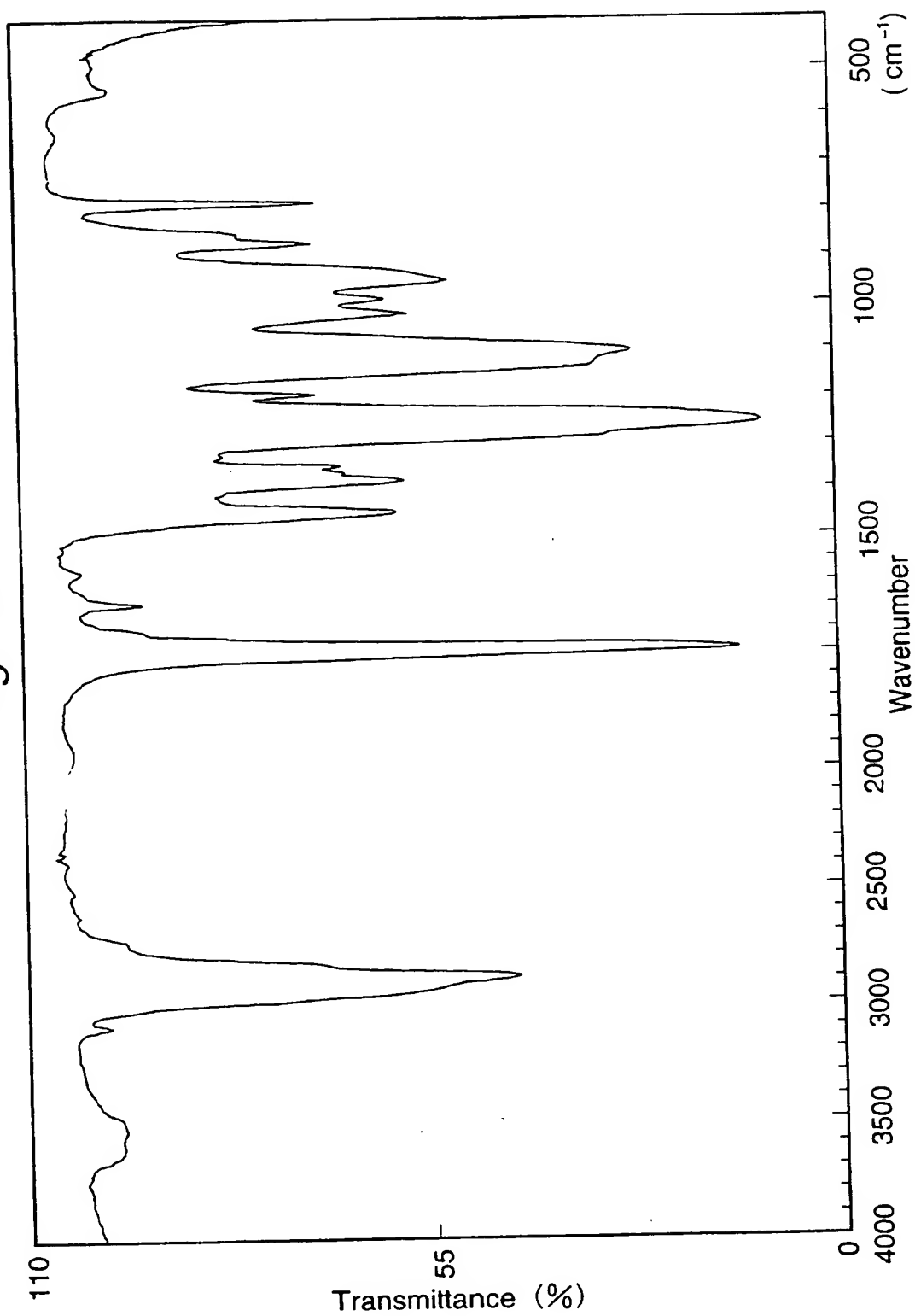


Fig. 9

Fig. 10



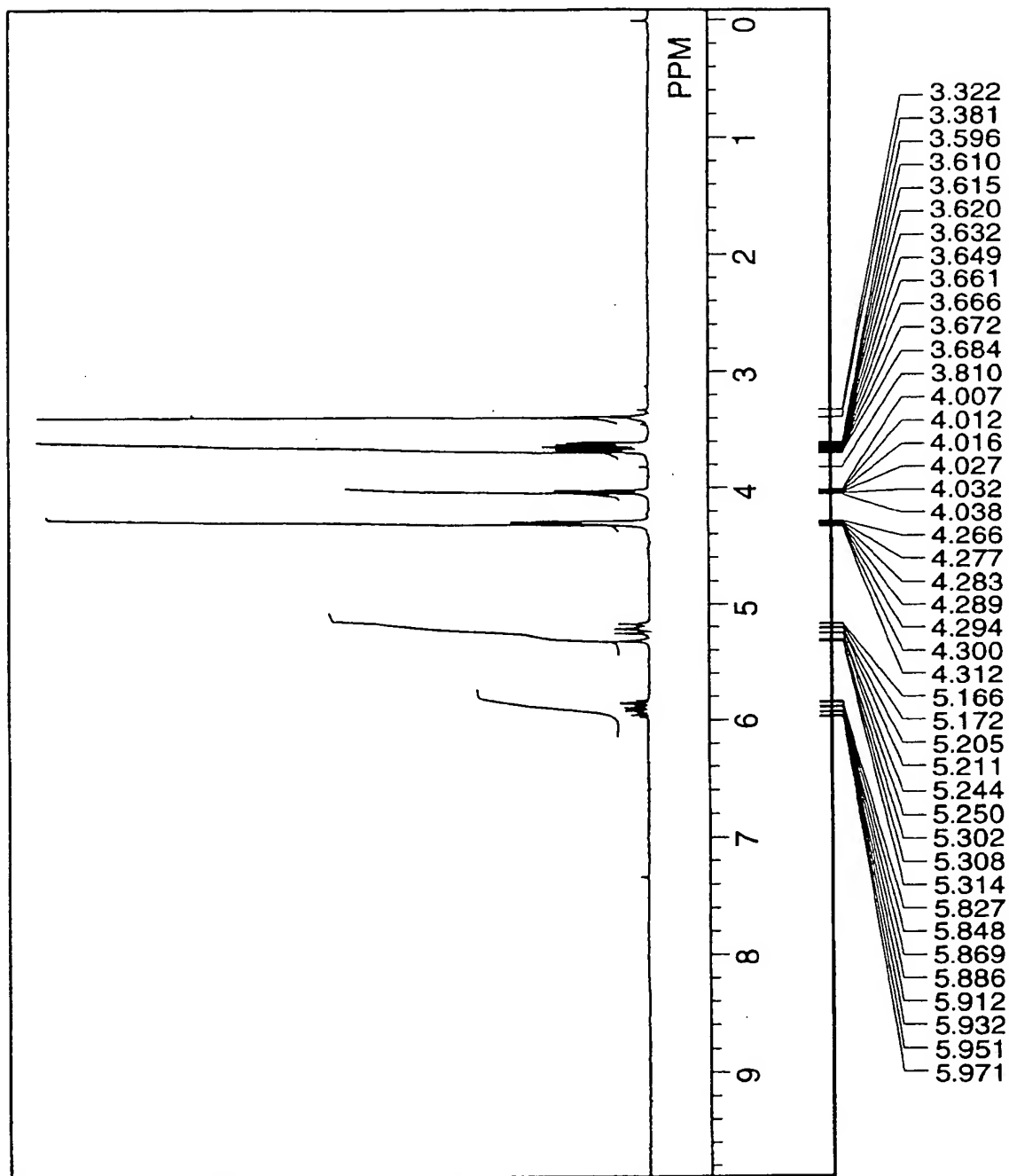


Fig. 12

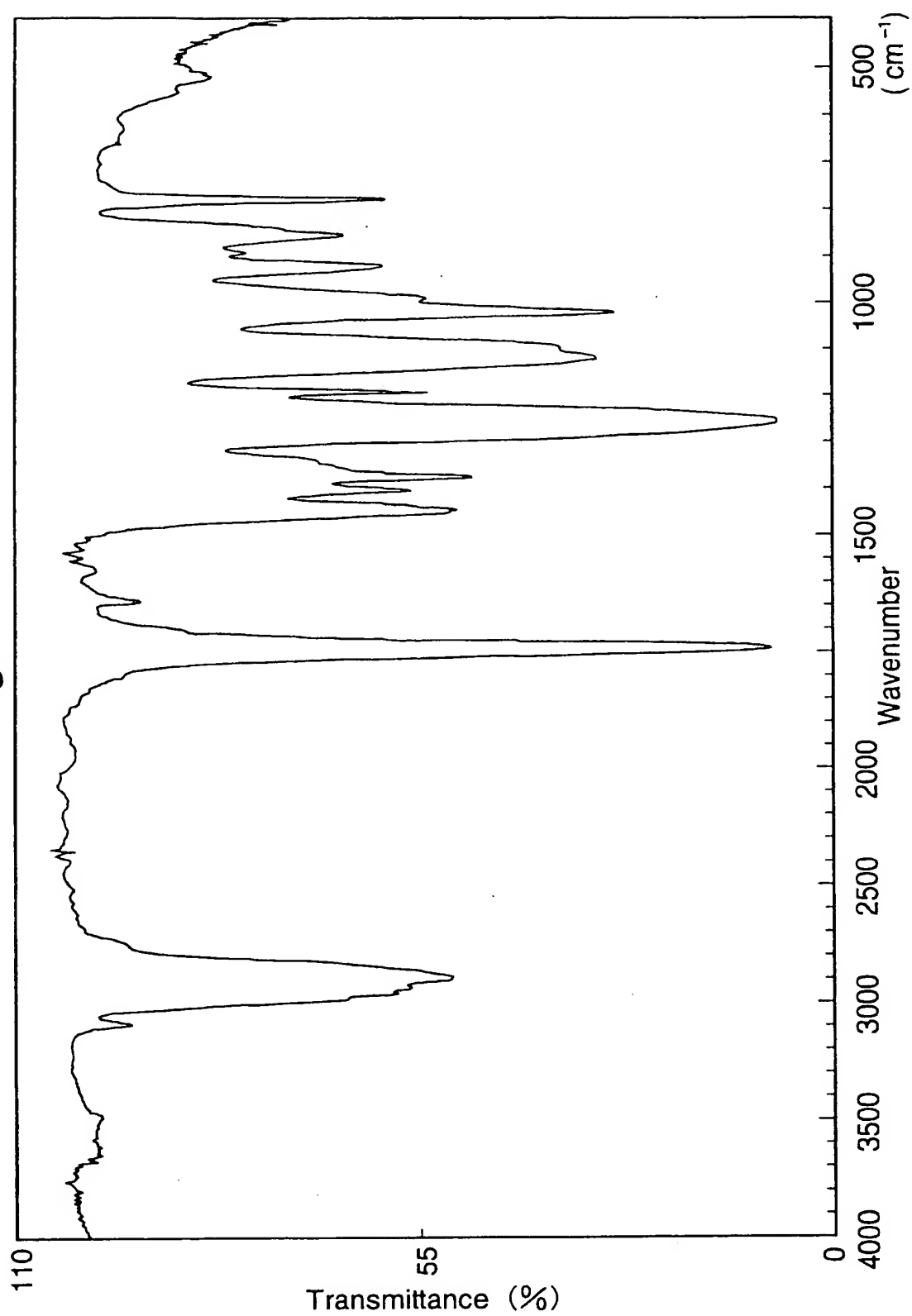
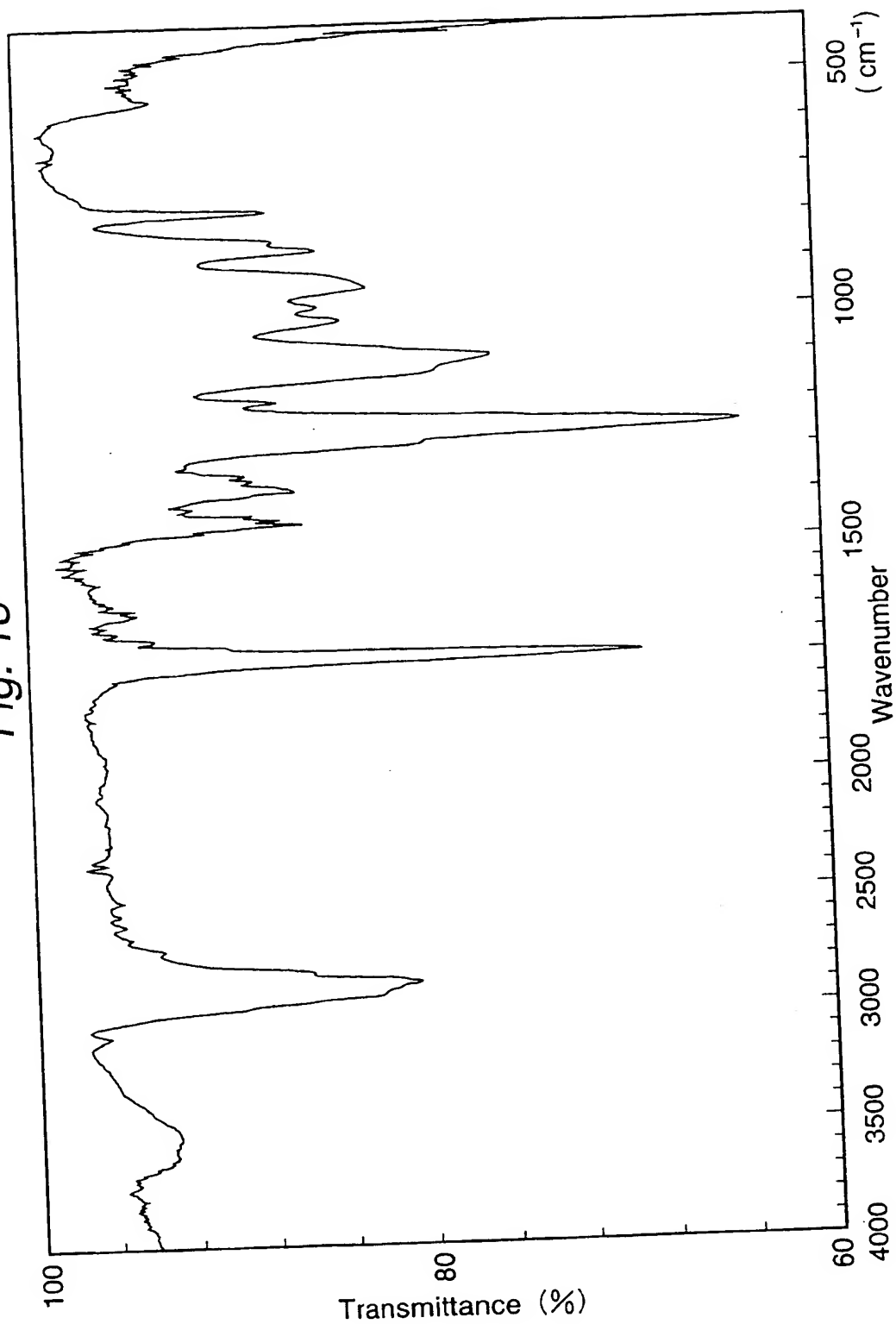


Fig. 13



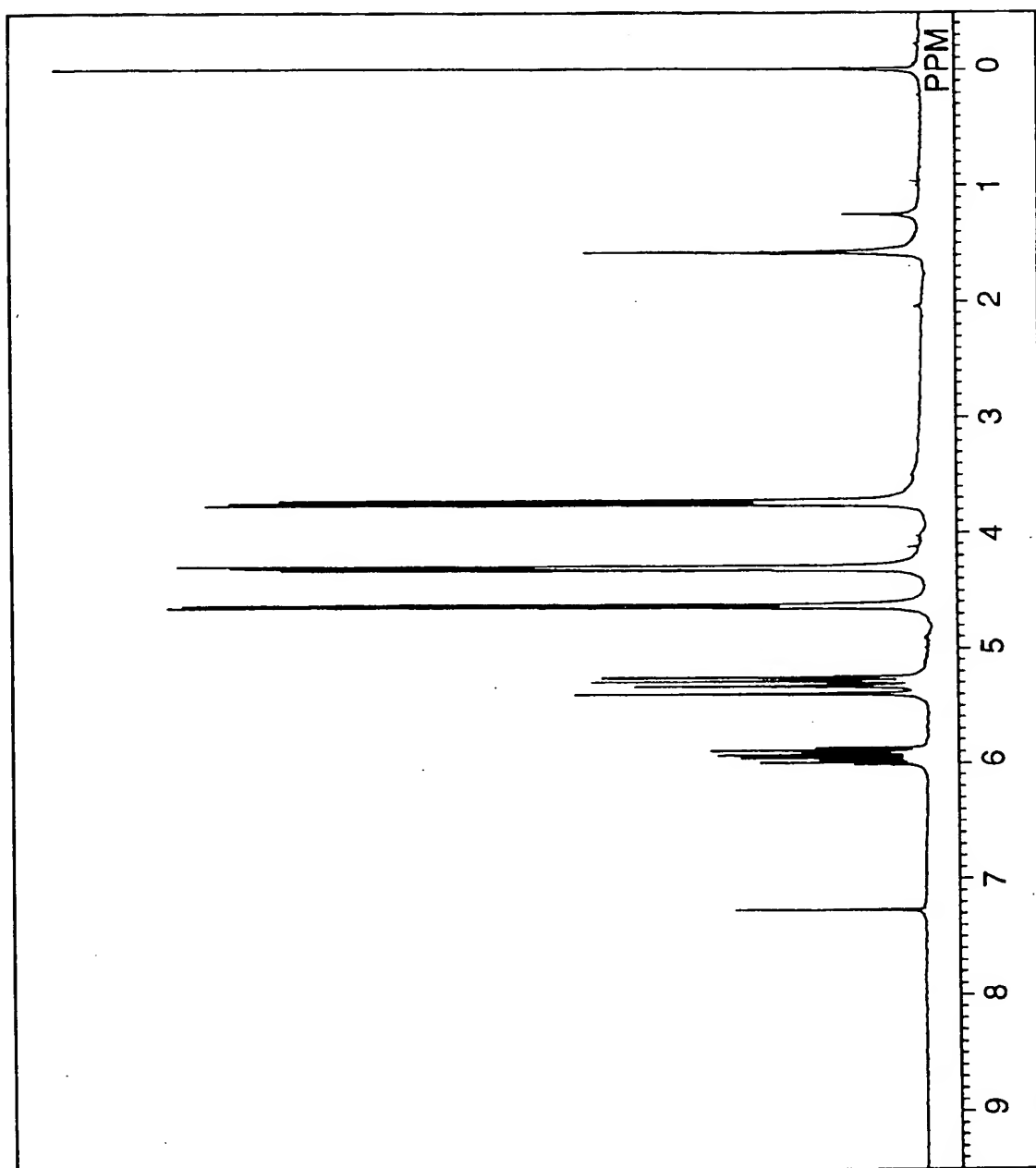


Fig. 14

Fig. 15

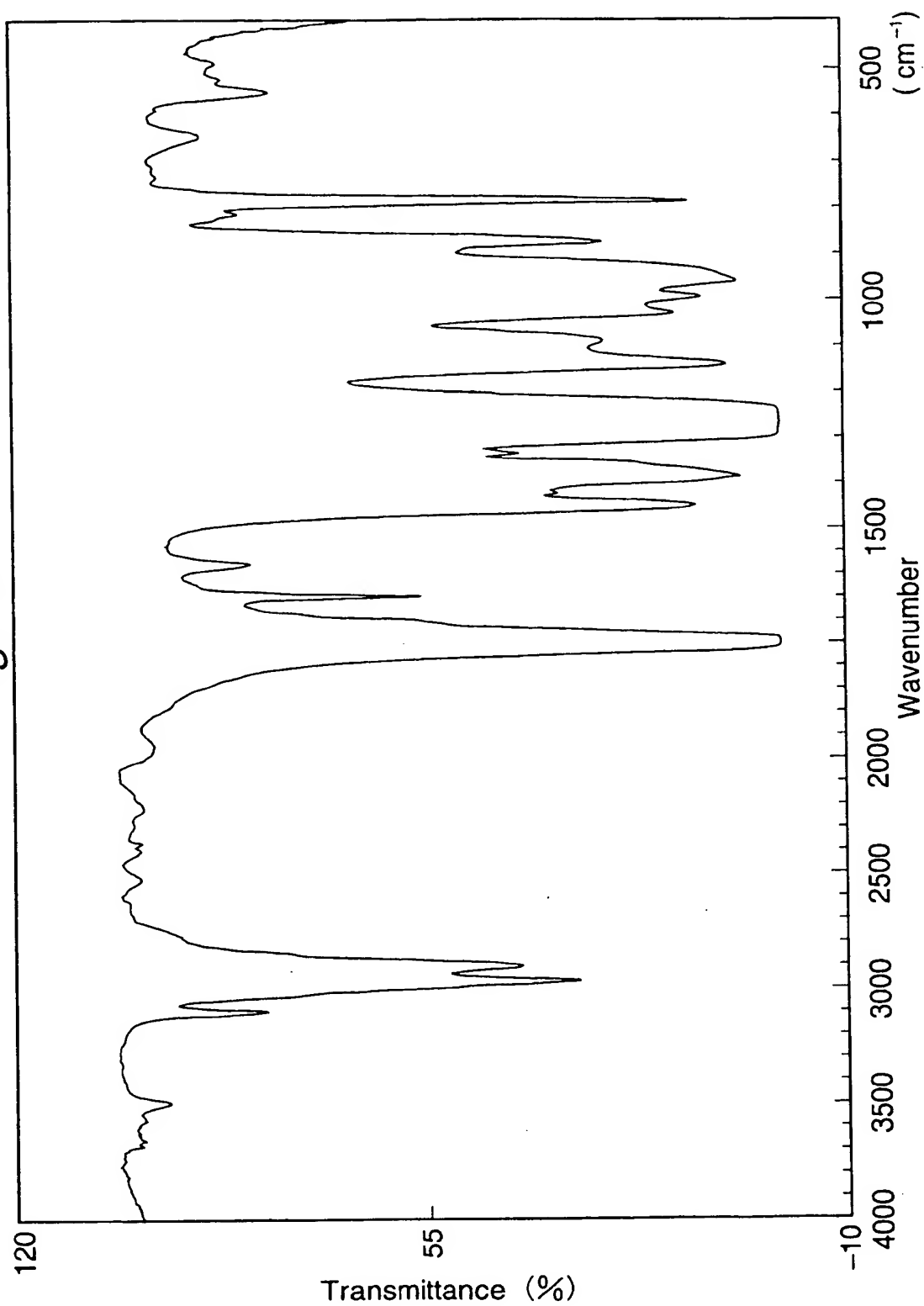
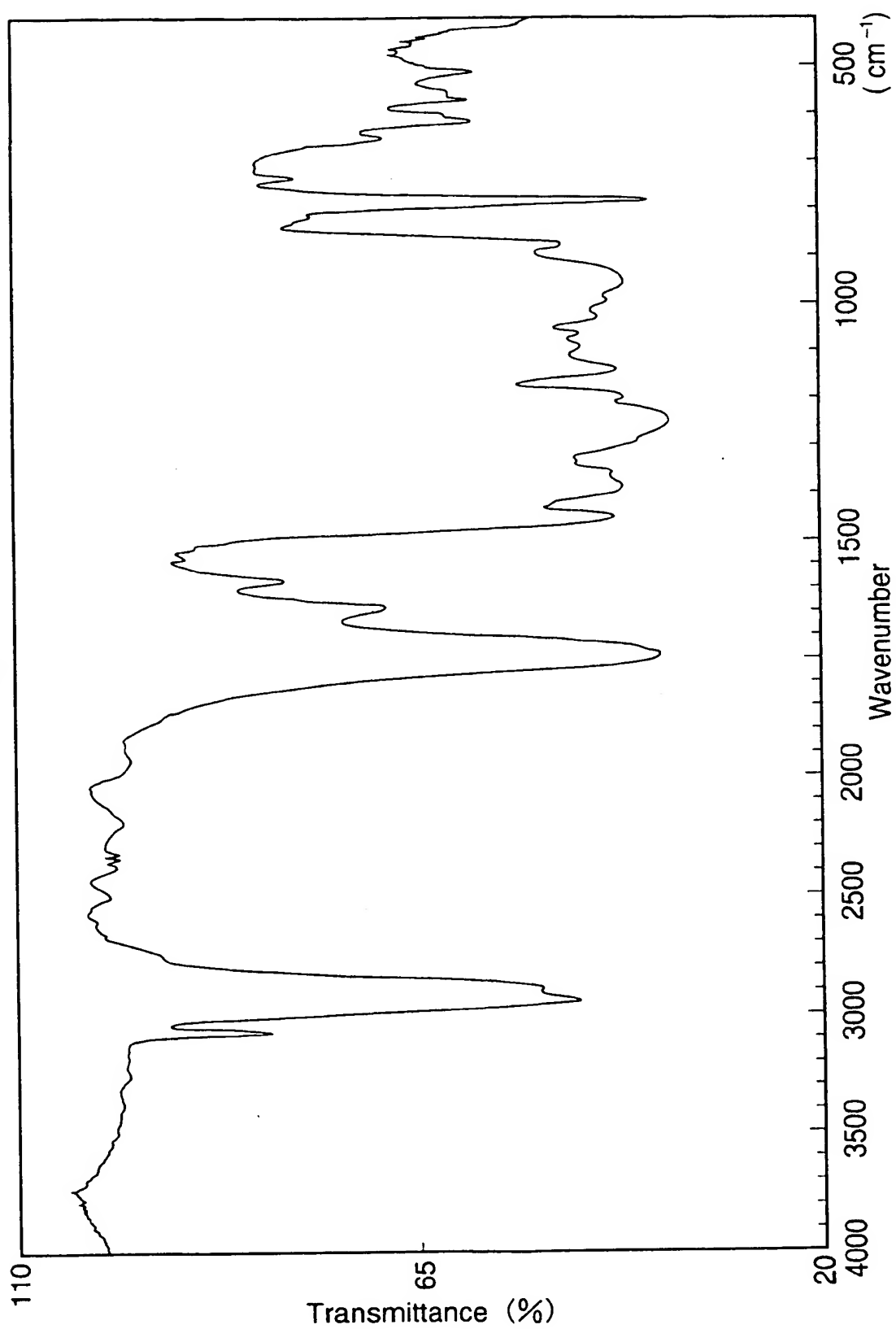


Fig. 16



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/02358

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl⁶ C08F16/26, 18/24, 20/28, 299/00, C08G65/32, C07C69/96,
H01B1/12, H01M10/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl⁶ C08F16/26, 116/12, 216/12, 18/24, 118/00, 218/00, 20/28,
120/28, 220/28, 299/00, C08G65/32, C07C69/96, H01B1/12, H01M10/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 1-249807, A (Mitsui Petrochemical Industries, Ltd.), October 5, 1989 (05. 10. 89), Claim (Family: none)	4, 14, 15
X	JP, 2-86642, A (Mitsui Petrochemical Industries, Ltd.), March 27, 1990 (27. 03. 90), Claim (Family: none)	4, 14, 15
X	JP, 57-135816, A (Mobil Oil Corp.), August 21, 1982 (21. 08. 82), Claim & US, 4344982, A	1, 5, 6
X	JP, 42-8292, B1 (Toagosei Chemical Industry Co., Ltd.), April 8, 1967 (08. 04. 67), Claim; page 1, right column, lines 24 to 26 (Family: none)	1, 5, 6
X	JP, 56-22710, A (Tokuyama Soda Co., Ltd.),	4, 14, 15

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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Date of the actual completion of the international search

November 14, 1996 (14. 11. 96)

Date of mailing of the international search report

November 26, 1996 (26. 11. 96)

Name and mailing address of the ISA/

Japanese Patent Office

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP96/02358

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	March 3, 1981 (03. 03. 81), Claim (Family: none)	
X	JP, 64-26620, A (Tokuyama Soda Co., Ltd.), January 27, 1989 (27. 01. 89), Claim (Family: none)	4, 14, 15
X	JP, 53-12813, A (Mitsubishi Gas Chemical Co., Inc.), February 4, 1978 (04. 02. 78), Page 1, right column, lines 7 to 15 (Family: none)	4, 14, 15
X	JP, 52-10395, A (Institut Khimicheskoi Fizic Akademiinauk SSSR), January 26, 1977 (26. 01. 77), Claim; page 4 & US, 4076742, A	2, 8, 9
A	JP, 7-263026, A (Yuasa Corp.), October 13, 1995 (13. 10. 95) (Family: none)	1 - 20
A	JP, 2-274728, A (Fuji Photo Film Co., Ltd.), November 8, 1990 (08. 11. 90) (Family: none)	1 - 20
A	JP, 8-295711, A (Nippon Oil Co., Ltd.), November 12, 1996 (12. 11. 96) (Family: none)	1 - 20

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